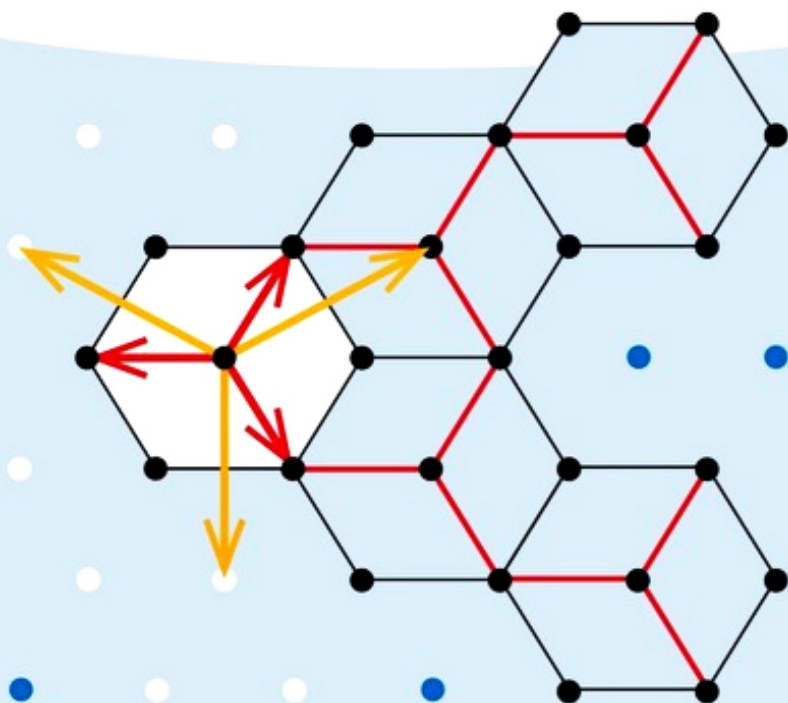


Wolfram Hergert and Matthias Geilhufe

Group Theory in Solid State Physics and Photonics

Problem Solving with Mathematica



*Wolfram Hergert and
R. Matthias Geilhufe*

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Physics and Photonics**

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Problem Solving with Mathematica

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Contents

Preface *XI*

1 Introduction *1*

1.1 Symmetries in Solid-State Physics and Photonics *4*

1.2 A Basic Example: Symmetries of a Square *6*

Part One Basics of Group Theory *9*

2 Symmetry Operations and Transformations of Fields *11*

2.1 Rotations and Translations *11*

2.1.1 Rotation Matrices *13*

2.1.2 EULER Angles *16*

2.1.3 EULER–RODRIGUES Parameters and Quaternions *18*

2.1.4 Translations and General Transformations *23*

2.2 Transformation of Fields *25*

2.2.1 Transformation of Scalar Fields and Angular Momentum *26*

2.2.2 Transformation of Vector Fields and Total Angular Momentum *27*

2.2.3 Spinors *28*

3 Basics Abstract Group Theory *33*

3.1 Basic Definitions *33*

3.1.1 Isomorphism and Homomorphism *38*

3.2 Structure of Groups *39*

3.2.1 Classes *40*

3.2.2 Cosets and Normal Divisors *42*

3.3 Quotient Groups *46*

3.4 Product Groups *48*

4	Discrete Symmetry Groups in Solid-State Physics and Photonics	51
4.1	Point Groups	52
4.1.1	Notation of Symmetry Elements	52
4.1.2	Classification of Point Groups	56
4.2	Space Groups	59
4.2.1	Lattices, Translation Group	59
4.2.2	Symmorphic and Nonsymmorphic Space Groups	62
4.2.3	Site Symmetry, WYCKOFF Positions, and WIGNER–SEITZ Cell	65
4.3	Color Groups and Magnetic Groups	69
4.3.1	Magnetic Point Groups	69
4.3.2	Magnetic Lattices	72
4.3.3	Magnetic Space Groups	73
4.4	Noncrystallographic Groups, Buckyballs, and Nanotubes	75
4.4.1	Structure and Group Theory of Nanotubes	75
4.4.2	Buckminsterfullerene C_{60}	79
5	Representation Theory	83
5.1	Definition of Matrix Representations	84
5.2	Reducible and Irreducible Representations	88
5.2.1	The Orthogonality Theorem for Irreducible Representations	90
5.3	Characters and Character Tables	94
5.3.1	The Orthogonality Theorem for Characters	96
5.3.2	Character Tables	98
5.3.3	Notations of Irreducible Representations	98
5.3.4	Decomposition of Reducible Representations	102
5.4	Projection Operators and Basis Functions of Representations	105
5.5	Direct Product Representations	112
5.6	WIGNER–ECKART Theorem	120
5.7	Induced Representations	123
6	Symmetry and Representation Theory in k-Space	133
6.1	The Cyclic BORN–VON KÁRMÁN Boundary Condition and the BLOCH Wave	133
6.2	The Reciprocal Lattice	136
6.3	The BRILLOUIN Zone and the Group of the Wave Vector $\mathbf{k}$	137
6.4	Irreducible Representations of Symmorphic Space Groups	142
6.5	Irreducible Representations of Nonsymmorphic Space Groups	143

Part Two Applications in Electronic Structure Theory 149

- 7 Solution of the Schrödinger Equation 151**
 - 7.1 The SCHRÖDINGER Equation 151
 - 7.2 The Group of the SCHRÖDINGER Equation 153
 - 7.3 Degeneracy of Energy States 154
 - 7.4 Time-Independent Perturbation Theory 157
 - 7.4.1 General Formalism 159
 - 7.4.2 Crystal Field Expansion 160
 - 7.4.3 Crystal Field Operators 164
 - 7.5 Transition Probabilities and Selection Rules 169
- 8 Generalization to Include the Spin 177**
 - 8.1 The PAULI Equation 177
 - 8.2 Homomorphism between $SU(2)$ and $SO(3)$ 178
 - 8.3 Transformation of the Spin–Orbit Coupling Operator 180
 - 8.4 The Group of the PAULI Equation and Double Groups 183
 - 8.5 Irreducible Representations of Double Groups 186
 - 8.6 Splitting of Degeneracies by Spin–Orbit Coupling 189
 - 8.7 Time-Reversal Symmetry 193
 - 8.7.1 The Reality of Representations 193
 - 8.7.2 Spin-Independent Theory 194
 - 8.7.3 Spin-Dependent Theory 196
- 9 Electronic Structure Calculations 197**
 - 9.1 Solution of the Schrödinger Equation for a Crystal 197
 - 9.2 Symmetry Properties of Energy Bands 198
 - 9.2.1 Degeneracy and Symmetry of Energy Bands 200
 - 9.2.2 Compatibility Relations and Crossing of Bands 201
 - 9.3 Symmetry-Adapted Functions 203
 - 9.3.1 Symmetry-Adapted Plane Waves 203
 - 9.3.2 Localized Orbitals 205
 - 9.4 Construction of Tight-Binding Hamiltonians 210
 - 9.4.1 Hamiltonians in Two-Center Form 212
 - 9.4.2 Hamiltonians in Three-Center Form 216
 - 9.4.3 Inclusion of Spin–Orbit Interaction 224
 - 9.4.4 Tight-Binding Hamiltonians from *ab initio* Calculations 225
 - 9.5 Hamiltonians Based on Plane Waves 227
 - 9.6 Electronic Energy Bands and Irreducible Representations 230
 - 9.7 Examples and Applications 236
 - 9.7.1 Calculation of FERMI Surfaces 236
 - 9.7.2 Electronic Structure of Carbon Nanotubes 238
 - 9.7.3 Tight-binding Real-Space Calculations 240
 - 9.7.4 Spin–Orbit Coupling in Semiconductors 245
 - 9.7.5 Tight-Binding Models for Oxides 247

Part Three Applications in Photonics 251**10 Solution of Maxwell's Equations 253****10.1 MAXWELL's Equations and the Master Equation for Photonic Crystals 254****10.1.1 The Master Equation 254****10.1.2 One- and Two-Dimensional Problems 256****10.2 Group of the Master Equation 257****10.3 Master Equation as an Eigenvalue Problem 259****10.4 Models of the Permittivity 260****10.4.1 Reduced Structure Factors 264****10.4.2 Convergence of the Plane Wave Expansion 266****11 Two-Dimensional Photonic Crystals 269****11.1 Photonic Band Structure and Symmetrized Plane Waves 270****11.1.1 Empty Lattice Band Structure and Symmetrized Plane Waves 270****11.1.2 Photonic Band Structures: A First Example 273****11.2 Group Theoretical Classification of Photonic Band Structures 276****11.3 Supercells and Symmetry of Defect Modes 279****11.4 Uncoupled Bands 283****12 Three-Dimensional Photonic Crystals 287****12.1 Empty Lattice Bands and Compatibility Relations 287****12.2 An example: Dielectric Spheres in Air 291****12.3 Symmetry-Adapted Vector Spherical Waves 293****Part Four Other Applications 299****13 Group Theory of Vibrational Problems 301****13.1 Vibrations of Molecules 301****13.1.1 Permutation, Displacement, and Vector Representation 302****13.1.2 Vibrational Modes of Molecules 305****13.1.3 Infrared and Raman Activity 307****13.2 Lattice Vibrations 310****13.2.1 Direct Calculation of the Dynamical Matrix 312****13.2.2 Dynamical Matrix from Tight-Binding Models 314****13.2.3 Analysis of Zone Center Modes 315****14 Landau Theory of Phase Transitions of the Second Kind 319****14.1 Introduction to Landau's Theory of Phase Transitions 320****14.2 Basics of the Group Theoretical Formulation 324****14.3 Examples with GTPack Commands 326****14.3.1 Invariant Polynomials 326****14.3.2 LANDAU and LIFSHITZ Criterion 327**

Appendix A Spherical Harmonics 331

- A.1 Complex Spherical Harmonics 332
- A.1.1 Definition of Complex Spherical Harmonics 332
- A.1.2 Cartesian Spherical Harmonics 332
- A.1.3 Transformation Behavior of Complex Spherical Harmonics 333
- A.2 Tesseral Harmonics 334
- A.2.1 Definition of Tesseral Harmonics 334
- A.2.2 Cartesian Tesseral Harmonics 335
- A.2.3 Transformation Behavior of Tesseral Harmonics 336

Appendix B Remarks on Databases 337

- B.1 Electronic Structure Databases 337
- B.1.1 Tight-Binding Calculations 337
- B.1.2 Pseudopotential Calculations 338
- B.1.3 Radial Integrals for Crystal Field Parameters 339
- B.2 Molecular Databases 339
- B.3 Database of Structures 339

Appendix C Use of MPB together with GTPack 341

- C.1 Calculation of Band Structure and Density of States 341
- C.2 Calculation of Eigenmodes 342
- C.3 Comparison of Calculations with MPB and *Mathematica* 343

Appendix D Technical Remarks on GTPack 345

- D.1 Structure of GTPack 345
- D.2 Installation of GTPack 346

References 349**Index 359**

Preface

Symmetry principles are present in almost all branches of physics. In solid-state physics, for example, we have to take into account the symmetry of crystals, clusters, or more recently detected structures like fullerenes, carbon nanotubes, or quasicrystals. The development of high-energy physics and the standard model of elementary particles would have been unimaginable without using symmetry arguments. Group theory is the mathematical approach used to describe symmetry. Therefore, it has become an important tool for physicists in the past century.

In some cases, understanding the basic concepts of group theory can become a bit tiring. One reason is that exercises connected to the definitions and special structures of groups as well as applications are either trivial or become quickly tedious, even if the concrete calculations are mostly elementary. This occurs, especially, when a textbook does not offer additional help and special tools to assist the reader in becoming familiar with the content. Therefore, we chose a different approach for the present book. Our intention was not to write another comprehensive text about group theory in solid-state physics, but a more applied one based on the *Mathematica* package GTPack. Therefore, the book is more a handbook on a computational approach to group theory, explaining all basic concepts and the solution of symmetry-related problems in solid-state physics by means of GTPack commands. With the length of the manuscript in mind, we have, at some points, omitted longer and rather technical proofs. However, the interested reader is referred to more rigorous textbooks in those cases and we provide specific references. The examples and tasks in this book are supposed to encourage the reader to work actively with GTPack.

GTPack itself provides more than 200 additional modules to the standard *Mathematica* language. The content ranges from basic group theory and representation theory to more applied methods like crystal field theory and tight-binding and plane-wave approaches to symmetry-based studies in the fields of solid-state physics and photonics. GTPack is freely available online via GTPack.org. The package is designed to be easily accessible by providing a complete *Mathematica* style documentation, an optional input validation, and an error strategy. Therefore, we believe that also advanced users of group theory concepts will benefit from the book and the *Mathematica* package. We provide a compact reference material and a programming environment that will help to solve actual research problems in an efficient way.

In general, computer algebra systems (CAS) allow for a symbolic manipulation of algebraic expressions. Modern systems combine this basic property with numerical algorithms and visualization tools. Furthermore, they provide a programming language for the implementation of individual algorithms. In principle, one has to distinguish between general purpose systems like, e.g., *Mathematica* and *Maple*, and systems developed for special purposes. Although the second class of systems usually has a limited range of applications, it aims for much better computational performance. The *GAP* system (Groups, Algorithms, and Programming) is one of these specialized systems and has a focus on group theory. Extensions like the system *Cryst*, which was built on top of *GAP*, are specialized in terms of computations with crystallographic groups.

Nevertheless, for this book we decided to use *Mathematica*, as *Mathematica* is well established and often included in the teaching of various Physics departments worldwide. At the Department of Physics of the Martin Luther University Halle-Wittenberg, for example, specialized *Mathematica* seminars are provided to accompany the theoretical physics lectures. In these courses, *GTPack* has been used actively for several years.

During the development of *GTPack*, two paradigms were followed. First, in the usual *Mathematica* style, the names of commands should be intuitive, i.e., from the name itself it should become clear what the command is supposed to be applied for. This also implies that the nomenclature corresponds to the language physicists usually use in solid-state physics. Second, the commands should be intuitive in their application. Unintentional misuse should not result in longer error messages and endless loop calculations but in an abort with a precise description of the error itself. To distinguish *GTPack* commands from the standard *Mathematica* language, all commands have a prefix **GT** and all options a prefix **GO**. Analogously to *Mathematica* itself, commands ending with **Q** result in logical values, i.e., either TRUE or FALSE. For example, the new command **GTGroupQ**[*list*] checks if a *list* of elements forms a group.

The combination of group theory in physics and *Mathematica* is not new in its own sense. For example, the books of EL-BATANOUNY and WOOTEN [1] and MC-CLAIN [2] also follow this concept. These books provide many code examples of group theoretical algorithms and additional material as a CD or on the Internet. However, in contrast to these books, we do not concentrate on the presentation of algorithms within the text, but provide well-established algorithms within the *GTPack* modules. This maintains the focus on the application and solution of real physics problems. References for the implemented algorithms are provided whenever appropriate.

In addition to applications in solid-state physics we also discuss photonics, a field that has undergone rapid development over the last 20 years. Here, instead of discussing the symmetry properties of the SCHRÖDINGER, PAULI, or DIRAC equations, MAXWELL's equations are in the focus of consideration. Analogously to the periodic crystal lattice in solids, periodically structured dielectrics are discussed. *GTPack* can be applied in a similar manner to both fields.

The book itself is structured as follows. After a short introduction, the basic aspects of group theory are discussed in Part One. Part Two covers the application of group theory to electronic structure theory, whereas Part Three is devoted to its application to photonics. Finally, in Part Four two additional applications are discussed to demonstrate that GTPack will be helpful also for problems other than electronic structure and photonics.

GTPack has a long history in terms of its development. In this context, we would like to thank Diemo Ködderitzsch, Markus Däne, Christian Matyssek, and Stefan Thomas for their individual contributions to the package. We would especially like to acknowledge the careful work of Sebastian Schenk, who contributed significantly to the implementation of the documentation system. Furthermore, we would like to thank Kalevi Kokko, Turku University Finland, who provided a silent work place for us on several occasions. At his department, we had the opportunity to concentrate on both the book and the package and many parts were completed in this context. This was a big help. We acknowledge general interest and support from Martin Hoffmann and Arthur Ernst. Also we would like to thank Wiley-VCH, especially Waltraud Wüst, Martin Preuss and Stefanie Volk.

Lastly, we would like to thank our families for their patience and support during this long-term project.

Stockholm and Halle (Saale),
October 2017

R. Matthias Geilhufe, Wolfram Hergert

1

Introduction

When the original German version was first published in 1931, there was a great reluctance among physicists toward accepting group theoretical arguments and the group theoretical point of view. It pleases the author, that this reluctance has virtually vanished in the meantime and that, in fact, the younger generation does not understand the causes and the bases of this reluctance.

E.P. Wigner (Group Theory, 1959)

Symmetry is a far-reaching concept present in mathematics, natural sciences and beyond. Throughout the chapter the concept of symmetry and symmetry groups is motivated by specific examples. Starting with symmetries present in nature, architecture, fine arts and music a transition will be made to solid state physics and photonics and the symmetries which are of relevance throughout this book. Finally the square is taken as a first explicit example to explore all transformations leaving this object invariant.

Symmetry and symmetry breaking are important concepts in nature and almost every field of our daily life. In a first and general approach symmetry might be defined as: *Symmetry is present when one cannot determine any change in a system after performing a structural or any other kind of transformation.*

Nature, Architecture, Fine Arts, and Music

One of the most fascinating examples for symmetry in nature is the manifold and beauty of the mineral skeletons of Radiolaria, which are tiny unicellular species. Figure 1.1a shows a table from HAECKEL's "Art forms in Nature" [4] presenting a special group of Radiolaria called Spumellaria.

The concept of symmetry can also be found in architecture. Our urban environment is characterized by a mixture of buildings of various centuries. However, every epoch reflects at least some symmetry principles. For example, the Art déco style buildings, like the Chrysler Building in New York City (cf. Figure 1.1b), use symmetry as a design element in a particularly striking manner.

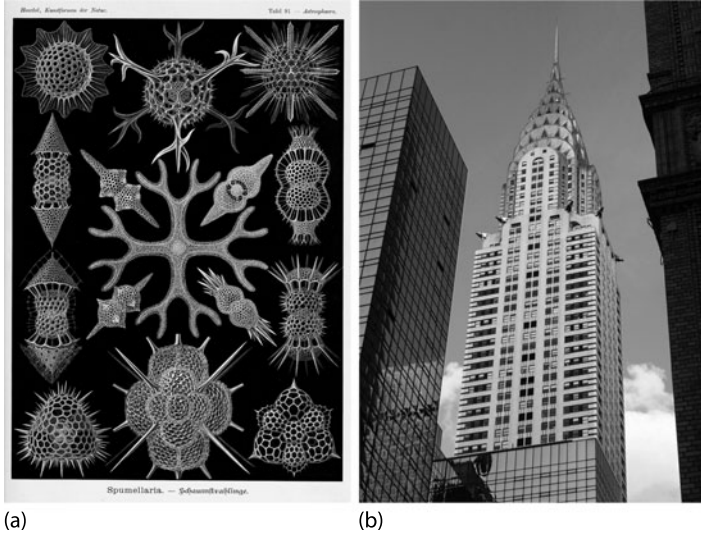


Figure 1.1 Symmetry in nature and architecture. (a) Table 91 from HAECKEL's 'Art forms in Nature' [4]; (b) Chrysler Building in New York City [5] (© JORGE ROYAN, www.royan.com.ar, CC BY-SA 3.0).

Within the fine arts, the works of M.C. ESCHER (1898–1972) gain their special attraction from an intellectually deliberate confusion of symmetry and symmetry breaking.

In ESCHER's woodcut Snakes [6], a threefold rotational symmetry can be easily detected in the snake pattern. A rotation by 120° transforms the painting into itself. A considerable amount of his work is devoted to mathematical principles and symmetry. The series "Circle Limits" deals with hyperbolic regular tessellations, but they are also interesting from the symmetry point of view. The woodcut, entitled Circle Limit III [6], the most interesting under the four circle limit woodcuts, shows a twofold rotational axis. If the figure is transformed into a black and white version a fourfold rotational axis appears. Obviously, the color leads to a reduction of symmetry [7]. The change of symmetry by inclusion of additional degrees of freedom like color in the present example or the spin, if we consider a quantum mechanical system, leads to the concept of color or SHUBNIKOV groups. A comprehensive overview on symmetry in art and sciences is given by SHUBNIKOV [8]. WEYL [9] and ALTMANN [10] start their discussion of symmetry principles from a similar point of view.

Also in music symmetry principles can be found. Tonal and temporal reflections, translations, and rotations play an important role. J.S. BACH's crab canon from *The Musical Offering* (BWV1079) is an example for reflection. The brilliant effects in M. RAVEL's Boléro achieved by a translational invariant theme represent an impressive example as well.

Physics

The conservation laws in classical mechanics are closely related to symmetry. Table 1.1 gives an overview of the interplay between symmetry properties and the resulting conservation laws.

A general formulation of this connection is given by the NOETHER theorem. That symmetry principles are the primary features that constrain dynamical laws was one of the great advances of EINSTEIN in his *annus mirabilis* 1905 [11]. The relevance of symmetry in all fields of theoretical physics can be seen as a major achievement of twentieth century physics.

In parallel to the development of quantum theory, the direct connection between quantum theory and group theory was understood. Especially E. WIGNER revealed the role of symmetry in quantum mechanics and discussed the application of group theory in a series of papers between 1926 and 1928 [11] (see also H. WEYL 1928 [12]). Symmetry accounts for the degeneracy of energy levels of a quantum system. In a central field, for example, an energy level should have a degeneracy of $2l + 1$ (l – angular momentum quantum number) because the angular momentum is conserved due to the rotational symmetry of the potential. However, considering the hydrogen atom a higher ‘accidental’ symmetry can be found, where levels have a degeneracy of n^2 , the square of the principle quantum number. The reason was revealed by PAULI [13, 14] in 1926 using the conservation of the quantum mechanical analogue of the LENZ–RUNGE vector and by FOCK in 1935 by the comparison of the SCHRÖDINGER equation in momentum space with the integral equation of four-dimensional spherical harmonics [15]. FOCK showed that the electron effectively moves in an environment with the symmetry of a hypersphere in four-dimensional space. The symmetry of the hydrogen atom is mediated by transformations of the entire Hamiltonian and not of its parts, the kinetic and the potential energy alone. Such *dynamical symmetries* cannot be found by the analysis of forces and potentials alone. The basic equations of quantum theory and electromagnetism are time dependent, i.e., dynamic equations. Therefore, the symmetry properties of the physical systems as well as the symmetry properties of the fundamental equations have to be taken into account.

Table 1.1 Conservation laws and symmetry in classical mechanics.

Symmetry property	Conserved quantity
Homogeneity of time (translations in time)	⇒ Energy
Homogeneity of space (translations in space)	⇒ Momentum
Isotropy of space (rotations in space)	⇒ Angular momentum
Invariance under GALILEI transformations	⇒ Center of gravity

1.1

Symmetries in Solid-State Physics and Photonics

In Figure 1.2, two representative examples of solid-state systems are shown. The scanning tunneling microscope (STM) image in Figure 1.2a depicts two monolayers of MgO on a Ag(001) surface in atomic resolution. The quadratic arrangement of protrusions representing one sublattice is clearly revealed. One of the main tasks of solid-state theory is the calculation of the electronic structure of systems starting from the real-space structure.

However, the many-particle SCHRÖDINGER equation, containing the coordinates of all nuclei and electrons of a solid cannot be solved directly, neither analytically nor numerically. This problem can be approached by discussing effective one-particle systems, for example, in the framework of density functional theory (cf. [16]). Therefore, it will be sufficient to study SCHRÖDINGER-like equations in the following to investigate implications of crystal symmetry.

In the first years of electronic structure theory of solids, principles of group theory were applied to optimize computations of complex systems as much as possible due to the limited computational resources available at that time. Although this aspect becomes less important nowadays, the connection between symmetry in the structure and the electronic properties is one of the main applications of group theory.

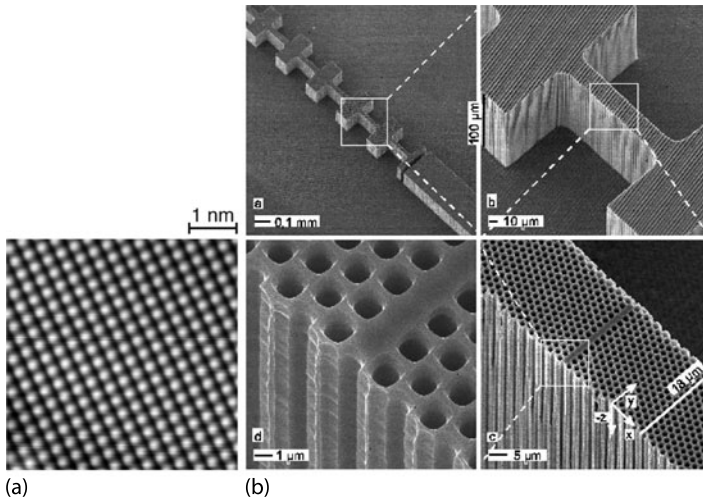


Figure 1.2 Symmetry in solid-state physics and photonics. (a) Atomically resolved STM image of two monolayers of MgO on Ag(001) (from [17], Figure 1) (With permission, Copyright © 2017 American Physical Society.) (b) SEM image of a width-modulated

stripe (a) of macroporous silicon on a silicon substrate. The increasing magnification in (b)–(d) reveals a waveguide structure prepared by a missing row of pores. (from [18]). (With permission, Copyright © 1999 Wiley-VCH GmbH.)

Next to the optimization of numerical calculations, group theory can be applied to classify promising systems for further investigations, like in the case of the search for multiferroic materials [19, 20]. In general, four primary ferroic properties are known: ferroelectricity, ferromagnetism, ferrotoroidicity, and ferroelasticity. The magnetoelectric coupling, of special interest in applications, is a secondary ferroic effect. The occurrence of multiple ferroic properties in one phase is connected to specific symmetry conditions a material has to accomplish.

Defects in solids and at solid surfaces play a continuously increasing role in basic research and applications (diluted magnetic semiconductors, p -magnetism in oxides). For example, group theory allows to get useful information in a general and efficient way (cf. [21, 22]) treating defect states in the framework of perturbation theory.

More recently, a close connection between high-energy physics and condensed matter physics has been established, where effective elementary excitations within a crystal behave as particles that were formally described in elementary particle physics. A promising class of materials are Dirac materials like graphene, where the elementary electronic excitations behave as relativistic massless Dirac fermions [23, 24]. Degeneracies and crossings of energy bands within the electronic band structure together with the dispersion relation in the neighborhood of the crossing point are closely related to the crystalline symmetry [25, 26].

In Figure 1.2b, a scanning electron microscope (SEM) image of macroporous silicon is shown. The special etching technique provides a periodically structured dielectric material that is referred to as a photonic crystal. The propagation of electromagnetic waves in such structures can be calculated starting from MAXWELL's equations [27, 28]. The resulting eigenmodes of the electromagnetic field are closely connected to the symmetry of the structured dielectric. Group theory can be applied in various cases within the field of photonics. Subsequently, a few examples are mentioned. The photonic bands of two-dimensional photonic crystals can be classified with respect to the symmetry of the lattice. The symmetry properties of the eigenmodes, found by means of group theory, decide whether this mode can be excited by an external plane wave [29]. Metamaterials are composite materials that have peculiar electromagnetic properties that are different from the properties of their constituents. Group theory can be used for design and optimization of such materials [30]. Group theoretical arguments also help to discuss the dispersion in photonic crystal waveguides in advance. Clearly, this approach represents a more sophisticated strategy in comparison to relying on a trial and error approach [31, 32]. If a magneto-optical material is used for a photonic crystal, time-reversal symmetry is broken due to the intrinsic magnetic field. In this case, the theory of magnetic groups can be used to study the properties of such systems [33].

The goal of this book is to discuss the variety of possible applications of computational group theory as a powerful tool for actual research in photonics and electronic structure theory. Specific examples using the *Mathematica* package GT-Pack will be provided.

1.2

A Basic Example: Symmetries of a Square

As a first example, the symmetry of a square is discussed (Figure 1.3). The square is located in the xy -plane. In general, the whole xy -plane could be covered completely by squares leading to a periodic arrangement like that of the STM image from the two MgO layers on Ag(001) in Figure 1.2a. Subsequently, operations that leave the square invariant are identified.¹⁾

First, *rotations* of $0, \pi/2, \pi$, and $3\pi/2$ in the mathematical positive direction around the z -axis represent such operations. A rotation by an angle of 0° induces no change at all and is therefore named *identity element* E . Instead of the rotation by $3\pi/2$ a rotation by $-\pi/2$ can be considered. Furthermore, a rotation by an angle of $\varphi + n2\pi$, $n = 1, 2, \dots$ is equivalent to a rotation by φ and is not considered as a new operation. In total, four inequivalent rotational operations are found.

Next to rotations leaving the square invariant, *reflection lines* can be identified. Performing a reflection, the perpendicular coordinates with respect to the line change their sign. In the present example, the x -axis is such a reflection line and furthermore a symmetry operation. By a reflection along this line, the point 1 becomes 4, 2 becomes 3, and vice versa. If the symmetries are considered in three dimensions, a reflection might be expressed by a rotation with angle π around the normal direction of the reflection line (here it is the y -axis) followed by an *inversion* (the inversion changes the signs of *all* coordinates). A rotation around the y -axis interchanges the points 1 and 2 and 4 and 3 as well. After applying an inversion the points 1 and 3 and 2 and 4 are interchanged. Additionally, the y -axis and the two diagonals of the square are reflection lines.

In total there are eight inequivalent symmetry elements, four rotations and four reflections. Those elements form the *symmetry group* of the square. The combination of two symmetry elements, i.e., the application one after another, leads to another element of the group.

In Figure 1.4, a square is presented with different coloring schemes. It can be verified that the use of color in Figure 1.4b–d reduces the symmetry. The symmetry groups of the colored squares are *subgroups* of the group of the square of

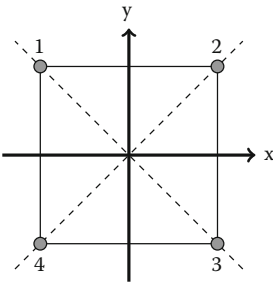


Figure 1.3 Square with coordinate system and reflection lines. The vertices are numbered only to explain the effect of symmetry operations.

1) Symmetry operations are restricted here to the xy -plane, i.e., are orthogonal coordinate transformations in x and y represented by 2×2 matrices.

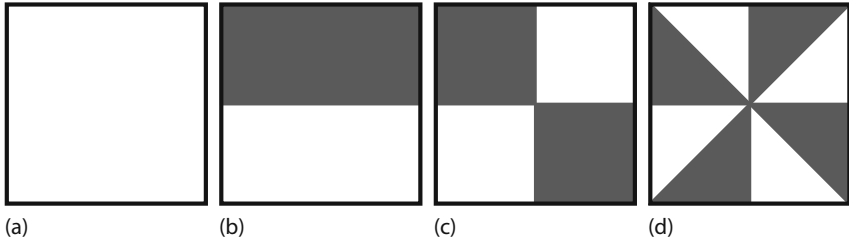


Figure 1.4 Symmetry of a square: Square colored in different ways.

Figure 1.4a. As an example: In Figure 1.4c the diagonal reflection lines still exist, but the mirror symmetry along the x - and y -axis is broken. Furthermore, the fourfold rotation axis is reduced to a twofold rotation axis. While the square itself represents a geometrical symmetry, the color scheme might be thought to be connected with a physical property like the spin, in terms of spin-up (black) and spin-down (white).

In the next sections, the basics of group theory are introduced. The symmetry group of the square will be kept as an example. Referring to Figure 1.2b, a hexagonal arrangement of pores can be seen for the photonic crystal. The symmetry group of a hexagon has 12 elements.

Task 1 (Symmetry of the square and the hexagon). The Notebook `GTTTask_1.nb` contains a discussion of the symmetry properties of the colored squares of Figure 1.4. Extend the discussion to a regular hexagon and its different colored versions to get familiar with *Mathematica* and GTPack.

Part One

Basics of Group Theory

2

Symmetry Operations and Transformations of Fields

Wer die Bewegung nicht kennt, kennt die Natur nicht.

Aristoteles (Phys. III; 1 200b 15–16)

The symmetry of a physical system is described by operations leaving the system invariant. Throughout the chapter such operations are introduced and discussed. In general, symmetry operations can be distinguished in rotations and translations. Furthermore, rotations can be subdivided into proper and improper rotations depending on the sign of the determinant of the rotation matrix. Besides rotation matrices, alternative representations of rotations can be derived. In particular, EULER angles, EULER–RODRIGUES parameters and quaternions are discussed. Many physical theories like electrodynamics and quantum mechanics are field theories. To provide a basic framework for later chapters, the transformation properties of scalar, vector and spinor fields are derived.

2.1

Rotations and Translations

Rotations, EULER angles, quaternions	
GTRestallAxes	Change between active and passive definition of transformations
GTWhichAxes	Prints whether active or passive definition is used
GTEulerAnglesQ	Checks if the input is a list of EULER angles
GTGetEulerAngles	Gives EULER angles for a given symmetry element
GTQuaternionQ	Checks if the input is a quaternion
GTQMultiplication	Multiplication of quaternions
GTQInverse	Gives the inverse of a quaternion
GTQAbs	Gives the absolute value of a quaternion
GTQConjugate	Gives the conjugate of a quaternion
GTQPolar	Gives the polar angle of a quaternion

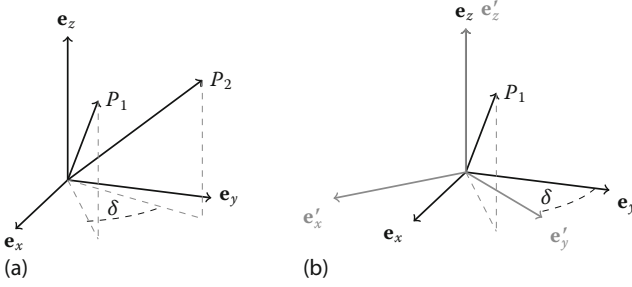


Figure 2.1 Illustration of active and passive rotation. (a) Active rotation; (b) passive rotation.

A coordinate transformation in three-dimensional Euclidean space $\mathbb{R}^3$ can be written as a combination of a pure rotation or reflection and a translation. Such transformations can be discussed as *active* or *passive* (Figure 2.1). Subsequently, both terms will be explained for pure rotations. A Cartesian coordinate system, fixed in space, is given in terms of the mutually orthogonal unit vectors $(\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z)$. A vector $\mathbf{r}_1$ points from the origin O to the point P_1 . An *active* rotation moves the point P_1 to P_2 and the vector $\mathbf{r}_1$ is transformed to $\mathbf{r}_2$ satisfying $|\mathbf{r}_1| = |\mathbf{r}_2|$

$$\mathbf{r}_2 = \hat{R}_z^{(a)}(\delta) \mathbf{r}_1. \quad (2.1)$$

Here, $\hat{R}_z^{(a)}(\delta)$ represents the corresponding rotational operator, discussed in detail in Section 2.1.1, where the superscript indicates the active nature of the rotation and the subscript the rotation axis $\mathbf{e}_z$. A rotation about an angle δ in the mathematical positive sense (counterclockwise) is performed. The inverse of this operation is an operation around the same axis but by an angle $-\delta$, or, alternatively, by an angle δ but about the opposite direction of the rotation axis

$$\left(\hat{R}_z^{(a)}\right)^{-1}(\delta) = \hat{R}_z^{(a)}(-\delta) = \hat{R}_{-z}^{(a)}(\delta). \quad (2.2)$$

Hence, P_2 can be transformed to P_1 by the *inverse* operation

$$\mathbf{r}_1 = \left(\hat{R}_z^{(a)}\right)^{-1}(\delta) \mathbf{r}_2. \quad (2.3)$$

In comparison to active rotations, a *passive* rotation is defined by a rotation of the coordinate frame itself. Hence, by fixing a point P_1 with vector $\mathbf{r}_1$, and rotating to a new coordinate frame $(\mathbf{e}_{x'}, \mathbf{e}_{y'}, \mathbf{e}_{z'})$, the rotation can be formulated as

$$\mathbf{r}'_1 = \hat{R}_z^{(p)}(\delta) \mathbf{r}_1. \quad (2.4)$$

Even though the rotations (2.1) (active) and (2.4) (passive) are not equivalent, they can be related to each other. There is a one-to-one correspondence, or an isomorphism (in the group theory language), between both formulations

$$\hat{R}_z^{(a)}(\delta) = \hat{R}_z^{(p)}(-\delta), \quad \left(\hat{R}_z^{(a)}\right)^{-1}(\delta) = \hat{R}_z^{(a)}(-\delta) = \hat{R}_z^{(p)}(\delta). \quad (2.5)$$

A similar concept also applies for translations. In the active formulation, a point P_2 gets shifted to P_3 by a vector $\mathbf{t}$. In the passive formulation, the origin O of a rotated coordinate frame is shifted to O' by a vector $-\mathbf{t}$.

The calculation of physical, i.e., measurable quantities, is independent of choosing the active or passive formulation. Therefore, both conventions can be found in different references. For example, the books of CORNWELL [35, 36] and EL-BATANOUNY and WOOTEN [1] use the passive definition, while the active formulation is used by INUI *et al.* [37]. See also ALTMAN [38] and MORISSON and PARKER [39] for a detailed discussion of the topic.

Within GTPack the passive definition is used as the standard setting. Therefore, with the exception of this chapter, the *passive* formulation will be used throughout this book. The superscripts (a) and (p) are suppressed in the following as long as no specific reason for their use is present.

Example 1 (Active and passive rotations in GTPack). As a standard, GTPack uses the passive formulation of rotations. That means, asking for the rotation matrix of a symmetry element (e.g., a threefold rotation about $\mathbf{e}_z$, denoted by C_{3z}) using the command **GTGetMatrix** gives a matrix describing a clockwise rotation of the coordinate system about the z -axis. However, GTPack offers the option to switch between active and passive definition by means of the command **GTRinstallAxes**. An example is shown in Figure 2.2. To check which formulation is currently used, **GTWhichAxes** can be applied.

2.1.1

Rotation Matrices

Throughout this section, the active formulation of rotations will be used to discuss rotations in more detail. A rotation of a vector preserves the length of the vector itself and leaves the angle between any two transformed vectors invariant. Such a transformation (cf. Figure 2.3) is represented by an orthogonal matrix, i.e., also the operator $\hat{R}_z^{(a)}(\delta)$ is represented by an orthogonal matrix. A matrix is orthogonal if the columns (or rows) form an orthonormal set. The eigenvalues of orthogonal matrices are of absolute value 1. They are either real or appear in conjugate complex pairs. If the first column of a 2-dimensional matrix is given by the normalized vector $(\cos \varphi, \sin \varphi)$, two choices for the second column are possible satisfying the orthogonality of the matrix,

$$\underline{\underline{R}}_1 = \begin{pmatrix} \cos \varphi & -\sin \varphi \\ \sin \varphi & \cos \varphi \end{pmatrix}, \quad \underline{\underline{R}}_2 = \begin{pmatrix} \cos \varphi & \sin \varphi \\ \sin \varphi & -\cos \varphi \end{pmatrix}. \quad (2.6)$$

The determinants of these two matrices are ± 1 ,

$$\det \underline{\underline{R}}_1 = 1, \quad \det \underline{\underline{R}}_2 = -1. \quad (2.7)$$

Rotations with a determinant +1 are called *proper rotations*. Accordingly, rotations with a determinant -1 are called *improper rotations*. The eigenvalues of $\underline{\underline{R}}_1$

Mathematica**GTReinstallAxes, GTWhichAxes**

By default, the passive definition of rotations is used in GTPack as can be checked with **GTWhichAxes**.

```
In[8]:= GTWhichAxes[]
passive definition
```

Get the rotation matrix of C_{3z} in passive definition.

```
In[9]:= c3zp = GTGetMatrix[C3z]; c3zp // MatrixForm
```

```
Out[9]/MatrixForm=
```

$$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Switch to the active definition.

```
In[10]:= GTReinstallAxes["active"];
```

```
In[11]:= c3za = GTGetMatrix[C3z]; c3za // MatrixForm
```

```
Out[11]/MatrixForm=
```

$$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Both rotation matrices are inverse to each other.

```
In[12]:= c3za.c3zp // MatrixForm
```

```
Out[12]/MatrixForm=
```

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Figure 2.2 Change from the passive definition to the active definition of rotations by means of **GTReinstallAxes**.

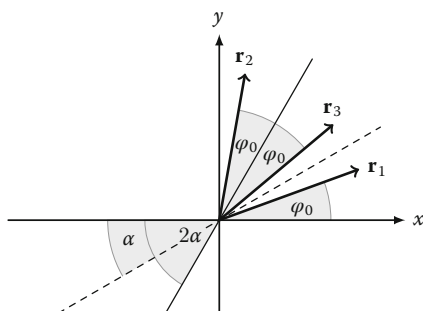


Figure 2.3 Result of the rotation by means of the matrices (2.6) on the vector r_1 .

and $\underline{\mathbb{R}}_2$, respectively, are given by

$$r_1^1 = \cos \varphi - i \sin \varphi, \quad r_2^1 = \cos \varphi + i \sin \varphi \quad (2.8)$$

and

$$r_1^2 = -1, \quad r_2^2 = +1. \quad (2.9)$$

Now, a vector $\mathbf{r}_1 = (r_0 \cos \varphi_0, r_0 \sin \varphi_0)$ being transformed under $\underline{\mathbb{R}}_1$ and $\underline{\mathbb{R}}_2$ with an angle $\varphi = 2\alpha$ is considered. The results of the transformations are

$$\mathbf{r}_2 = \underline{\mathbb{R}}_1 \cdot \mathbf{r}_1 = r_0 \begin{pmatrix} \cos(\alpha + (\alpha + \varphi_0)) \\ \sin(\alpha + (\alpha + \varphi_0)) \end{pmatrix}, \quad (2.10)$$

$$\mathbf{r}_3 = \underline{\mathbb{R}}_2 \cdot \mathbf{r}_1 = r_0 \begin{pmatrix} \cos(\alpha + (\alpha - \varphi_0)) \\ \sin(\alpha + (\alpha - \varphi_0)) \end{pmatrix}, \quad (2.11)$$

as can be seen in Figure 2.3. Matrix $\underline{\mathbb{R}}_1$ rotates $\mathbf{r}_1$ counterclockwise by an angle $\varphi = 2\alpha$. Hence, it is a proper rotation. In case of $\underline{\mathbb{R}}_2$, the vector $\mathbf{r}_1$ is getting reflected along a line with angle α to the x -axis. This *reflection* represents an improper rotation.

The equations (2.6) can be extended to the three-dimensional space, via

$$\underline{\mathbb{R}}'_1 = \begin{pmatrix} \cos \varphi & -\sin \varphi & 0 \\ \sin \varphi & \cos \varphi & 0 \\ 0 & 0 & c \end{pmatrix}, \quad \underline{\mathbb{R}}'_2 = \begin{pmatrix} \cos \varphi & \sin \varphi & 0 \\ \sin \varphi & -\cos \varphi & 0 \\ 0 & 0 & c \end{pmatrix}. \quad (2.12)$$

To obtain orthogonal matrices the parameter c has to be ± 1 . For $c = 1$, $\underline{\mathbb{R}}'_1$ and $\underline{\mathbb{R}}'_2$ represent the same transformations as before.

For $c = -1$, the transformation $\underline{\mathbb{R}}'_1$ represents a so-called *rotoreflexion*. That means, with respect to x and y the transformation is a proper rotation, but the z -component changes sign. Unlike $\underline{\mathbb{R}}_2$, the determinant of the matrix $\underline{\mathbb{R}}'_1$ is $+1$ for $c = -1$. The transformation $\underline{\mathbb{R}}'_2$ represents a *binary rotation* meaning a rotation by π around a certain axis. Here, the axis of rotation is *not the z -axis* as will be discussed in Task 2.

On the basis of properties of orthogonal matrices the following cases are possible for 3×3 transformation matrices:

- The matrix has one real and two conjugate complex eigenvectors (type A).
- All eigenvectors of the matrix are real (type B).

The various kinds of rotations are summarized in Table 2.1. The set of all proper and improper rotations forms a group called $O(3)$, the group of all three-dimensional orthogonal matrices. The subset of all proper rotations, i.e., 3-dimensional orthogonal matrices with determinant 1 forms the group $SO(3)$. The definition of a group is given in Chapter 3.

Table 2.1 The different cases of general rotations. The set of eigenvectors of type A contains one real and two mutually complex conjugate eigenvectors, while set B contains real eigenvectors only (complex conjugation is denoted by *).

Eigenvectors	Eigenvalues			Determinant	Operation
	a_1	a_2	a_3		
Type A	1	ω	ω^*	+1	Proper rotation
	-1	ω	ω^*	-1	Rotoreflexion (improper rotation)
Type B	1	1	1	+1	Identity
	1	1	-1	-1	Reflection
	1	-1	-1	+1	Binary rotation
	-1	-1	-1	-1	Inversion

2.1.2

EULER Angles

In general, every rotation can be expressed by a series of three rotations characterized by the EULER angles.

Definition 1 (EULER angles). A rotation $\underline{R}(\alpha, \beta, \gamma)$ can be described in the active convention by three successive rotations. A rotation of the system $\bar{\mathbf{e}}_x, \bar{\mathbf{e}}_y, \bar{\mathbf{e}}_z$ (or a vector $\mathbf{r}$) with respect to the coordinate system $\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z$ fixed in space is defined as:

- a rotation of $\bar{\mathbf{e}}_x, \bar{\mathbf{e}}_y, \bar{\mathbf{e}}_z$ by γ around $\mathbf{e}_z$,
- a rotation of the transformed $\bar{\mathbf{e}}_x, \bar{\mathbf{e}}_y, \bar{\mathbf{e}}_z$ by β around $\mathbf{e}_y$,
- finally a rotation of the transformed $\bar{\mathbf{e}}_x, \bar{\mathbf{e}}_y, \bar{\mathbf{e}}_z$ by α around $\mathbf{e}_z$.

The angles are restricted to:

$$-\pi < \gamma \leq \pi, \quad 0 \leq \beta \leq \pi, \quad -\pi < \alpha \leq \pi. \quad (2.13)$$

Mathematica GTEulerAnglesQ
<pre>In[1]:= GTEulerAnglesQ[{{0, 0, -2 \pi / 3}, 1}] Out[1]= True In[2]:= GTEulerAnglesQ[3] Out[2]= False</pre>

Figure 2.4 With the help of GTEulerAnglesQ it can be checked if the input is a list of EULER angles, $\{\alpha, \beta, \gamma\}$, $\det \underline{R}$.

Within GTPack EULER angles are implemented as lists of the form $\{\{\alpha, \beta, \gamma\}, \det \underline{\mathbb{R}}\}$. It is important to include the determinant of the rotation matrix, $\det \underline{\mathbb{R}}$ to also cover the set of improper rotations ($\det \underline{\mathbb{R}} = -1$). To check if an input is in the appropriate form used by GTPack, **GTEulerAnglesQ** can be applied. An example is shown in Figure 2.4.

According to the definition of the EULER angles, a rotation matrix can be written as the product of three orthogonal transformation matrices, describing rotations about the corresponding axes (cf. (2.12)),

$$\begin{aligned} \underline{\mathbb{R}}(\alpha, \beta, \gamma) &= \begin{pmatrix} \cos \alpha & -\sin \alpha & 0 \\ \sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos \beta & 0 & \sin \beta \\ 0 & 1 & 0 \\ -\sin \beta & 0 & \cos \beta \end{pmatrix} \begin{pmatrix} \cos \gamma & -\sin \gamma & 0 \\ \sin \gamma & \cos \gamma & 0 \\ 0 & 0 & 1 \end{pmatrix} \\ &= \begin{pmatrix} \cos \alpha \cos \beta \cos \gamma - \sin \alpha \sin \gamma & -\cos \alpha \cos \beta \sin \gamma - \sin \alpha \cos \gamma & \cos \alpha \sin \beta \\ \sin \alpha \cos \beta \cos \gamma + \cos \alpha \sin \gamma & -\sin \alpha \cos \beta \sin \gamma + \cos \alpha \cos \gamma & \sin \alpha \sin \beta \\ -\sin \beta \cos \gamma & \sin \beta \sin \gamma & \cos \beta \end{pmatrix}. \end{aligned} \quad (2.14)$$

However, the choice of EULER angles is not unique and the following relations can be verified,

$$\begin{aligned} \underline{\mathbb{R}}(\alpha, 0, \gamma) &= \underline{\mathbb{R}}(\alpha + \gamma, 0, 0) = \underline{\mathbb{R}}(0, 0, \alpha + \gamma), \\ \underline{\mathbb{R}}(\alpha, \pi, \gamma) &= \underline{\mathbb{R}}(\alpha + \delta, \pi, \gamma + \delta). \end{aligned} \quad (2.15)$$

Here, δ is an arbitrary angle. The inverse rotation $\underline{\mathbb{R}}(\alpha, \beta, \gamma)^{-1}$ is defined via,

$$\underline{\mathbb{R}}(\alpha, \beta, \gamma)^{-1} \cdot \underline{\mathbb{R}}(\alpha, \beta, \gamma) = \underline{\mathbb{1}}, \quad (2.16)$$

where $\underline{\mathbb{1}}$ denotes the identity matrix. The inverse matrix itself is given by

$$\underline{\mathbb{R}}(\alpha, \beta, \gamma)^{-1} = \underline{\mathbb{R}}(-\gamma \pm \pi, \beta, -\alpha \pm \pi) \quad (2.17)$$

The sign has to be chosen such that the angles are in agreement with (2.13).

The EULER angles can be determined from the components of a rotation matrix. For a given matrix $\underline{\mathbb{R}}$,

$$\underline{\mathbb{R}} = \begin{pmatrix} r_{11} & r_{12} & r_{13} \\ r_{21} & r_{22} & r_{23} \\ r_{31} & r_{32} & r_{33} \end{pmatrix} \quad (2.18)$$

the EULER angles can be deduced from (2.14),

$$\beta = \arccos r_{33}, \quad \gamma = -\arctan \left(\frac{r_{32}}{r_{31}} \right), \quad \alpha = \arctan \left(\frac{r_{23}}{r_{13}} \right). \quad (2.19)$$

Mathematica**GTGetEulerAngles**

In[8]:= **GTWhichAxes** []

active definition

Get Euler Angles from a rotation matrix (corresponds to C_{3z}).

In[9]:= **GTGetEulerAngles** [{ { - $\frac{1}{2}$, - $\frac{\sqrt{3}}{2}$, 0 }, { $\frac{\sqrt{3}}{2}$, - $\frac{1}{2}$, 0 }, { 0, 0, 1 } }]

Out[9]= { { 0, 0, $\frac{2\pi}{3}$ }, 1 }

Get Euler angles from symbols

In[10]:= **GTGetEulerAngles** [**C3z**]
GTGetEulerAngles [**C3zi**]

Out[10]= { { 0, 0, $\frac{2\pi}{3}$ }, 1 }

Out[11]= { { 0, 0, - $\frac{2\pi}{3}$ }, 1 }

Figure 2.5 Obtaining EULER angles from a matrix or a symbol using **GTGetEulerAngles**. The symbol C_{3z} denotes a counterclockwise rotation about the angle $2/3\pi$ about the z-axis.

Example 2 (EULER angles and GTPack). Within GTPack symmetry elements can be represented by symbols, matrices, EULER angles, or quaternions. Starting from symbols, matrices, or quaternions **GTGetEulerAngles** can be used to obtain an associated set of Euler angles. The application of the command is shown in Figure 2.5.

2.1.3

EULER-RODRIGUES Parameters and Quaternions

Historically, alternatives to 3×3 orthogonal matrices were introduced to describe rotations. Clearly, a rotation can be represented by a rotation axis and an angle φ ($-\pi \leq \varphi \leq +\pi$), where the axis is represented by a unit vector $\mathbf{n}$, the so-called *pole*. Per definition, a positive value of φ is assigned in the active formulation, if the rotation is counterclockwise, with respect to the direction of $\mathbf{n}$. The rotation parametrized by φ and $\mathbf{n}$ is written as $\hat{R}(\varphi, \mathbf{n})$, where the following relation holds,

$$\hat{R}(\varphi, \mathbf{n}) \equiv \hat{R}(-\varphi, -\mathbf{n}). \quad (2.20)$$

In the following, the relationship between rotation matrices and a representation by means of a pole and a rotation angle will be discussed (for more details see [38]).

- a) Obtaining a rotation matrix from φ and $\mathbf{n}$:

A skew-symmetric (or antisymmetric) matrix has the property

$$\underline{S}^T = -\underline{S}. \quad (2.21)$$

Therefore, the matrix $\underline{\underline{A}} = \exp(\underline{\underline{S}})$ is orthogonal. By choosing a skew-symmetric matrix $\underline{\underline{Z}}$ in terms of the components of the pole $\mathbf{n}$,

$$\underline{\underline{Z}} = \begin{pmatrix} 0 & -n_z & n_y \\ n_z & 0 & -n_x \\ -n_y & n_x & 0 \end{pmatrix}, \quad (2.22)$$

the rotation $\hat{R}(\varphi, \mathbf{n})$ can be written as

$$\begin{aligned} \hat{R}(\varphi, \mathbf{n}) &= \exp(\varphi \underline{\underline{Z}}) = \underline{\underline{I}} + \sin \varphi \underline{\underline{Z}} + (1 - \cos \varphi) \underline{\underline{Z}}^2 \\ &= \underline{\underline{I}} + \sin \varphi \underline{\underline{Z}} + 2 \sin^2(\varphi/2) \underline{\underline{Z}}^2. \end{aligned} \quad (2.23)$$

Substituting (2.22) in (2.23) leads to the matrix representation of $\underline{\underline{R}}(\varphi, \mathbf{n})$,

$$\underline{\underline{R}}(\varphi, \mathbf{n}) = \begin{pmatrix} 1 - 2(n_y^2 + n_z^2)c & -n_zs + 2n_xn_yc & n_ys + 2n_zn_xc \\ n_zs + 2n_xn_yc & 1 - 2(n_z^2 + n_x^2)c & -n_xs + 2n_yn_zc \\ -n_ys + 2n_zn_xc & n_xs + 2n_yn_zc & 1 - 2(n_x^2 + n_y^2)c \end{pmatrix} \quad (2.24)$$

where the abbreviations $s = \sin \varphi$, $c = \sin^2 \varphi/2$ are used. Furthermore, from equation (2.22) it follows $\underline{\underline{Z}} \cdot \mathbf{r} = \mathbf{n} \times \mathbf{r}$. Hence, the rotation of a vector $\mathbf{r}$ can be expressed as

$$\hat{R}(\varphi, \mathbf{n})\mathbf{r} = \mathbf{r} + \sin \varphi \mathbf{n} \times \mathbf{r} + 2 \sin^2(\varphi/2) \mathbf{n} \times (\mathbf{n} \times \mathbf{r}). \quad (2.25)$$

This transformation is known as the *conical transformation*, where the vector $\mathbf{r}$ rotates on a cone around the vector $\mathbf{n}$.

- b) Obtaining φ and $\mathbf{n}$ from a rotation matrix:

In general, a rotation matrix $\underline{\underline{R}}$ can be written as

$$\underline{\underline{R}} = \begin{pmatrix} r_{11} & r_{12} & r_{13} \\ r_{21} & r_{22} & r_{23} \\ r_{31} & r_{32} & r_{33} \end{pmatrix}. \quad (2.26)$$

In the following, proper rotations are considered, i.e., $\det \underline{\underline{R}} = 1$. The transformation of the rotation axis from an arbitrary axis to the z -axis represents a similarity transformation, $\underline{\underline{S}} \underline{\underline{R}} \underline{\underline{S}}^{-1}$. However, the trace of a matrix is invariant under similarity transformations. Hence, it is possible to verify

$$\begin{aligned} \text{Tr } \underline{\underline{R}} &= 2 \cos \varphi + 1 \\ \cos \varphi &= \frac{1}{2} (\text{Tr } \underline{\underline{R}} - 1). \end{aligned} \quad (2.27)$$

The rotation axis itself can be identified by finding an eigenvector with eigenvalue +1. Finally, the components of $\mathbf{n}$ can be expressed by the components of $\underline{\underline{R}}$, as follows from (2.24),

$$n_x = \frac{r_{32} - r_{23}}{2 \sin \varphi}, \quad n_y = \frac{r_{13} - r_{31}}{2 \sin \varphi}, \quad n_z = \frac{r_{21} - r_{12}}{2 \sin \varphi}. \quad (2.28)$$

Task 2 (Binary rotation). The rotation defined by the matrix

$$\underline{\mathbf{R}} = \begin{pmatrix} \cos \varphi & \sin \varphi & 0 \\ \sin \varphi & -\cos \varphi & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad (2.29)$$

is a binary rotation. Find the rotation axis and proof that $\underline{\mathbf{R}}$ describes a rotation of π around that axis. (The rotation axis is given by the eigenvector to eigenvalue $+1$.)

Definition 2 (EULER–RODRIGUES parameters). *The EULER–RODRIGUES parameters are the following combinations of φ and $\mathbf{n}$:*

$$\lambda = \cos \frac{\varphi}{2}, \quad \mathbf{\Lambda} = \sin \frac{\varphi}{2} \mathbf{n}. \quad (2.30)$$

A rotation expressed in terms of EULER–RODRIGUES parameters will be designated as $\hat{\mathbf{R}}(\lambda, \mathbf{\Lambda})$. The multiplication of two rotations is expressed as

$$\begin{aligned} \hat{\mathbf{R}}(\lambda_3, \mathbf{\Lambda}_3) &= \hat{\mathbf{R}}(\lambda_1, \mathbf{\Lambda}_1) \hat{\mathbf{R}}(\lambda_2, \mathbf{\Lambda}_2) \\ \lambda_3 &= \lambda_1 \lambda_2 - \mathbf{\Lambda}_1 \cdot \mathbf{\Lambda}_2, \quad \mathbf{\Lambda}_3 = \lambda_1 \mathbf{\Lambda}_2 + \lambda_2 \mathbf{\Lambda}_1 + \mathbf{\Lambda}_1 \times \mathbf{\Lambda}_2 \end{aligned} \quad (2.31)$$

Furthermore, the relations

$$\hat{\mathbf{R}}(\lambda, \mathbf{\Lambda}) = \hat{\mathbf{R}}(-\lambda, -\mathbf{\Lambda}) \quad (2.32)$$

$$\lambda^2 + \mathbf{\Lambda}^2 = \cos^2 \frac{\varphi}{2} + \sin^2 \frac{\varphi}{2} \mathbf{n} \cdot \mathbf{n} = 1 \quad (2.33)$$

hold.

Within GTPack rotations can be represented in terms of quaternions. The following definition of the quaternion algebra shows the similarity to the formulation of rotations by means of EULER–RODRIGUES parameters.

Definition 3 (Quaternion algebra). *A quaternion $\mathbb{A}$ is an object $[[a, \mathbf{A}]]$ consisting of a real scalar quantity a and a vector $\mathbf{A}$. Quaternions fulfill the noncommutative multiplication rule*

$$\mathbb{A}\mathbb{B} = [[a, \mathbf{A}]] [[b, \mathbf{B}]] = [[ab - \mathbf{A} \cdot \mathbf{B}, a\mathbf{B} + b\mathbf{A} + \mathbf{A} \times \mathbf{B}]]. \quad (2.34)$$

- The quaternion multiplication is associative.
- Quaternions of the form $[[a, 0]]$ are named real quaternions, because they act like real numbers:

$$[[a, 0]] [[b, 0]] = [[ab, 0]] \quad (2.35)$$

$$a [[b, \mathbf{B}]] = [[a, 0]] [[b, \mathbf{B}]] = [[ab, a\mathbf{B}]] \quad (2.36)$$

- A quaternion $[[0, \mathbf{A}]]$ is named a pure quaternion.

$$[[0, \mathbf{A}]] [[0, \mathbf{B}]] = [[-\mathbf{A} \cdot \mathbf{B}, \mathbf{A} \times \mathbf{B}]] \quad (2.37)$$

- A pure quaternion with a unit vector as the vectorial part is named a unit quaternion.

$$\mathbf{A} = |\mathbf{A}|\mathbf{n}, \quad \llbracket 0, \mathbf{A} \rrbracket = \llbracket 0, \mathbf{A}\mathbf{n} \rrbracket = \mathbf{A} \llbracket 0, \mathbf{n} \rrbracket \quad (2.38)$$

$$=_{\text{def}} \mathbf{A} \mathfrak{n} \quad (2.39)$$

- An additive formulation of quaternions is in agreement with the multiplication rule (2.34).

$$\llbracket a, \mathbf{A} \rrbracket = \llbracket a, 0 \rrbracket + \llbracket 0, \mathbf{A} \rrbracket \quad (2.40)$$

- It is possible to write quaternions in a binary form:

$$\llbracket a, \mathbf{A} \rrbracket = a + \mathbf{A} \mathfrak{n}, \quad \mathbf{A} = |\mathbf{A}| \quad (2.41)$$

- A quaternion may be expressed using the quaternion units

$$\mathfrak{i} = \llbracket 0, \mathbf{e}_x \rrbracket, \quad \mathfrak{j} = \llbracket 0, \mathbf{e}_y \rrbracket, \quad \mathfrak{k} = \llbracket 0, \mathbf{e}_z \rrbracket \quad (2.42)$$

$$\mathfrak{i}^2 = \mathfrak{j}^2 = \mathfrak{k}^2 = -1 \quad (2.43)$$

$$\mathfrak{i}\mathfrak{j} = \mathfrak{k}, \quad \mathfrak{j}\mathfrak{i} = -\mathfrak{k} \quad (2.44)$$

Therefore, the quaternion $\mathbb{A}$ can be written as

$$\mathbb{A} = \llbracket a, \mathbf{A} \rrbracket = a + A_x \mathfrak{i} + A_y \mathfrak{j} + A_z \mathfrak{k}. \quad (2.45)$$

The relationship between EULER–RODRIGUES parameters and quaternions is given by

$$\llbracket \lambda, \mathbf{\Lambda} \rrbracket = \left[\cos \frac{\varphi}{2}, \sin \frac{\varphi}{2} \mathbf{n} \right]. \quad (2.46)$$

Because of this connection a separate implementation of the EULER–RODRIGUES formalism is not necessary. If a rotation is represented by a quaternion $\mathbb{A} = \llbracket a, \mathbf{A} \rrbracket$ the corresponding matrix form is given by

$$\underline{\mathbf{R}} = \begin{pmatrix} a^2 + A_x^2 - A_y^2 - A_z^2 & 2(A_x A_y - a A_z) & 2(A_x A_z + a A_y) \\ 2(A_x A_y + a A_z) & a - A_x^2 + A_y^2 - A_z^2 & 2(A_y A_z - a A_x) \\ 2(A_x A_z - a A_y) & 2(A_y A_z + a A_x) & a^2 - A_x^2 - A_y^2 + A_z^2 \end{pmatrix}. \quad (2.47)$$

This result corresponds to the representation of the rotation matrix in terms of EULER–RODRIGUES parameters in (2.24).

Within GTPack quaternions are implemented in the form $\mathbb{A} \equiv \{\lambda, \{\Lambda_1, \Lambda_2, \Lambda_3\}\}$ as lists. With the help of **GTQuaternionQ**, it is possible to check if a given input is a quaternion as it is defined in GTPack. As shown in Figure 2.6, the multiplication of two quaternions according to equation (2.34) can be calculated by means of **GTQMultiplication** or by using the symbolic operator $\diamond$.¹⁾

1) In *Mathematica* this symbol can be obtained by typing `\[Diamond]` or by ESC dia ESC.

Mathematica
GTQuaternionQ, GTQMultiplication
<pre> In[9]:= q1 = {1/2, {0, 0, -sqrt(3)/2}}; q2 = {1/2, {-sqrt(3)/2, 0, 0}}; In[11]:= GTQuaternionQ[q1] Out[11]= True In[12]:= GTQMultiplication[q1, q2] Out[12]= {1/4, {-sqrt(3)/4, 3/4, -sqrt(3)/4}} In[13]:= q1 * q2 Out[13]= {1/4, {-sqrt(3)/4, 3/4, -sqrt(3)/4}} </pre>

Figure 2.6 The usage of GTQuaternionQ and GTQMultiplication in GTPack.

Mathematica
GTQInverse
<pre> In[14]:= q = {1/4, {-sqrt(3)/4, 3/4, -sqrt(3)/4}}; In[15]:= qi = GTQInverse[q] Out[15]= {1/4, {sqrt(3)/4, -3/4, sqrt(3)/4}} In[16]:= GTQMultiplication[q, qi] Out[16]= {1, {0, 0, 0}} </pre>

Figure 2.7 The application of GTQInverse.

For the multiplication operation an identity quaternion can be introduced, having the property $\mathbb{A}\mathbb{I} = \mathbb{A}$. It can be verified easily (see Task 3), that this quaternion has to be

$$\mathbb{I} = \llbracket 1, \mathbf{0} \rrbracket. \quad (2.48)$$

The inverse of a quaternion, satisfying the equation $\mathbb{A}\mathbb{A}^{-1} = \mathbb{I}$, is given by

$$\mathbb{A}^{-1} = \frac{\mathbb{A}^*}{|\mathbb{A}|^2}. \quad (2.49)$$

In the above equation, $\mathbb{A}^* = \llbracket a, -\mathbf{A} \rrbracket$ is called the conjugate quaternion of $\mathbb{A}$ and $|\mathbb{A}| = \sqrt{a^2 + \mathbf{A} \cdot \mathbf{A}}$ is the absolute value. With the help of GTPack the inverse of a

Mathematica GTQConjugate, GTQAbs, GTQPolar	
In[17]:=	$\mathbf{q} = \{1, \{1, 0, 0\}\}$
Out[17]=	$\{1, \{1, 0, 0\}\}$
In[18]:=	GTQConjugate [$\mathbf{q}$]
Out[18]=	$\{1, \{-1, 0, 0\}\}$
In[19]:=	GTQAbs [$\mathbf{q}$]
Out[19]=	$\sqrt{2}$
In[20]:=	GTQPolar [$\mathbf{q}$]
Out[20]=	$\frac{\pi}{4}$

Figure 2.8 The calculation of the conjugate quaternion, the absolute value of a quaternion, and the polar angle of a quaternion by means of **GTQConjugate**, **GTQAbs** and **GTQPolar**, respectively.

quaternion can be obtained by using the command **GTQInverse**. The application of **GTQInverse** is demonstrated in Figure 2.7.

The related commands to calculate the conjugate quaternion and the absolute value are **GTQConjugate** and **GTQAbs**, respectively. In equation (2.46), it is illustrated that the scalar part of a quaternion can be expressed by $\lambda = \cos(\varphi/2)$. Here, the angle φ is called the polar angle of the quaternion and can be calculated with **GTQPolar**. An example for **GTQConjugate**, **GTQAbs**, and **GTQPolar** can be found in Figure 2.8.

Task 3 (Working with quaternions). Use **GTPack** to verify

1. the identity quaternion is given by $\mathbb{I} = [\mathbb{I}, \mathbf{0}]$,
2. the inverse quaternion is given by $\mathbb{A}^{-1} = \frac{\mathbb{A}^*}{|\mathbb{A}|}$.

2.1.4

Translations and General Transformations

Previously, rotations and the corresponding rotation matrices were introduced. Subsequently, the product of two symmetry operations will be discussed. Here, T_1 and T_2 denote two abstract symmetry transformations and $\underline{\underline{R}}(T_1)$ and $\underline{\underline{R}}(T_2)$ their rotation matrices. By means of matrix multiplication, the product $T_1 \cdot T_2$ can be discussed via

$$T = T_2 \cdot T_1 \quad \Leftrightarrow \quad \underline{\underline{R}}(T) = \underline{\underline{R}}(T_2) \cdot \underline{\underline{R}}(T_1), \quad (2.50)$$

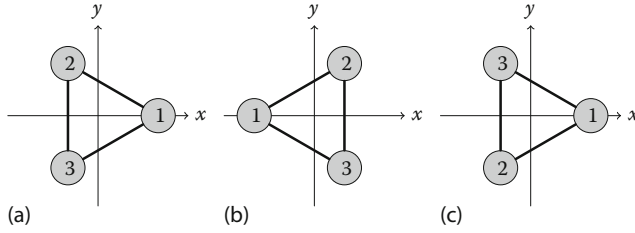


Figure 2.9 The symmetry transformation IC_{2y} applied to an equilateral triangle in the xy plane (Numbers are introduced to illustrate the impact of the operations.) (a) Triangle at the beginning; (b) two-fold rotation (rotation by an angle π) about the y -axis; (c) application of inversion I .

where $T = T_2 \cdot T_1$ can be understood as the application of T_2 after T_1 . For the transformation of a vector it follows

$$\mathbf{r}' = \underline{\underline{R}}(T_1)\mathbf{r}, \quad \mathbf{r}'' = \underline{\underline{R}}(T_2)\mathbf{r}' = \underline{\underline{R}}(T_2) \cdot \underline{\underline{R}}(T_1)\mathbf{r} = \underline{\underline{R}}(T)\mathbf{r}. \quad (2.51)$$

The following example will help to illustrate the concept.

Example 3 (Product of symmetry operations). A rotation of a triangle (cf. Figure 2.9) about the angle π about the y -axis (C_{2y}) is considered. Afterwards, an inversion I is applied. In terms of rotation matrices the operation $IC_{2y} = I \cdot C_{2y}$ is given as:

$$\begin{aligned} \underline{\underline{R}}(IC_{2y}) &= \underline{\underline{R}}(I) \cdot \underline{\underline{R}}(C_{2y}) \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} &= \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \cdot \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \end{aligned} \quad (2.52)$$

The two-fold rotation about the y -axis maps $x \rightarrow -x$, $y \rightarrow y$, and $z \rightarrow -z$. Hence, C_{2y} together with the inversion ($x \rightarrow -x$, $y \rightarrow -y$, and $z \rightarrow -z$) gives $x \rightarrow x$, $y \rightarrow -y$, and $z \rightarrow z$. The result is a reflection at the x - z plane (cf. also Table 2.1).

Theorem 1 (General transformation). A general symmetry transformation T consists of a rotation and a translation:

$$\begin{aligned} \mathbf{r}' &= \underline{\underline{R}}(T) \cdot \mathbf{r} + \mathbf{t}(T), \\ \mathbf{r}' &= \{ \underline{\underline{R}}(T) \mid \mathbf{t}(T) \} \mathbf{r}. \end{aligned} \quad (2.53)$$

By means of the short notation in (2.53) the product of two operations and the inverse can be formulated. If $T = T_2 \cdot T_1$, then

$$\{ \underline{\underline{R}}(T) \mid \mathbf{t}(T) \} = \{ \underline{\underline{R}}(T_2) \cdot \underline{\underline{R}}(T_1) \mid \underline{\underline{R}}(T_2) \cdot \mathbf{t}(T_1) + \mathbf{t}(T_2) \}. \quad (2.54)$$

The inverse transformation is given by

$$\{ \underline{\underline{R}}(T) \mid \mathbf{t}(T) \}^{-1} = \{ \underline{\underline{R}}(T^{-1}) \mid \mathbf{t}(T^{-1}) \} = \{ \underline{\underline{R}}^{-1}(T) \mid -\underline{\underline{R}}^{-1}(T)\mathbf{t}(T) \}. \quad (2.55)$$

Similarly to Theorem 1, a formulation in terms of the so-called *augmented matrix* can be used. The augmented matrix $\underline{\underline{W}}$ corresponding to a transformation $\{\underline{R}(T) | \mathbf{t}(T)\}$ is given (cf. [40]) by

$$\underline{\underline{W}} = \left(\begin{array}{ccc|c} & & & \\ & \underline{R}(T) & & \mathbf{t}(T) \\ \hline 0 & 0 & 0 & 1 \end{array} \right). \quad (2.56)$$

In GTPack general transformations are represented by means of angle brackets. For example, $\langle C_{4z}, \{-4, 1, 2\} \rangle$ is a general transformation consisting of the 4-fold rotation C_{4z} and the translation vector $\mathbf{t} = \{-4, 1, 2\}$.²⁾ The set of all transformations, consisting of all rotations of $O(3)$ together with all possible translations in $\mathbb{R}^3$, forms the so-called *Euclidean group* E_3 .

Task 4 (Augmented matrices). Proof that the augmented matrix (2.56) leads to the same transformation as defined in Theorem 1.

2.2

Transformation of Fields

Vectors, tensors, spinors	
GTSU2Matrix	Gives a rotation matrix in spin space for a given angle and a given rotation axis
GTGetSU2Matrix	Gives a rotation matrix in spin space for a given symmetry element

Physical theories like quantum mechanics or electrodynamics are field theories. The use of symmetry arguments requires the investigation of the properties of such fields under symmetry transformations. Electrodynamics represents the prototype for a classical field theory, where electric and magnetic fields are vector fields. The notation $\mathbf{E}(\mathbf{r}, t)$ for the electric field means that at time t a vector $\mathbf{E}$ is assigned to each point $\mathbf{r}$ in configuration space. Nonrelativistic quantum theory without spin is a scalar field theory. In terms of a general tensor field formulation the scalar field is a tensor field of rank 0, whereas the vector field is a tensor field of rank 1. If the quantum mechanical spin is included, the transformation properties of spinors have to be considered.

2) In *Mathematica*, the symbol $\langle$ is obtained by `\[LeftAngleBracket]` or `ESC<ESC`. Analogously, the symbol $\rangle$ is obtained.

2.2.1

Transformation of Scalar Fields and Angular Momentum

In the following, a scalar field $\psi(\mathbf{r})$, e.g., a solution of the stationary Schrödinger equation, is considered. A rotation $\mathbf{r}' = \underline{\underline{R}} \cdot \mathbf{r}$ in configuration space leads to the function $\tilde{\psi}(\mathbf{r})$, related to ψ by

$$\begin{aligned}\tilde{\psi}(\underline{\underline{R}} \cdot \mathbf{r}) &= \psi(\mathbf{r}), \\ \tilde{\psi}(\mathbf{r}) &= \psi(\underline{\underline{R}}^{-1} \cdot \mathbf{r}).\end{aligned}\quad (2.57)$$

In first order, an infinitesimal rotation $\delta\varphi$ about the axis $\mathbf{n}$ (cf. (2.25)) is approximated by

$$\hat{R}(\delta\varphi, \mathbf{n})\mathbf{r} = \mathbf{r} + \sin(\delta\varphi) \mathbf{n} \times \mathbf{r} + 2 \sin^2(\delta\varphi) \mathbf{n} \times \mathbf{n} \times \mathbf{r} \approx \mathbf{r} + \delta\varphi \mathbf{n} \times \mathbf{r}. \quad (2.58)$$

In terms of a Taylor series, an expansion of (2.58) with respect to the small change $\delta\varphi \mathbf{n} \times \mathbf{r}$ of the position vector leads to

$$\begin{aligned}\tilde{\psi}(\mathbf{r}) &= \psi(\mathbf{r}) - \delta\varphi (\mathbf{n} \times \mathbf{r}) \cdot \nabla \psi(\mathbf{r}), \\ &= \psi(\mathbf{r}) - \frac{i}{\hbar} \delta\varphi \mathbf{n} \cdot \left(\mathbf{r} \times \left(\frac{\hbar}{i} \nabla \right) \right) \psi(\mathbf{r}), \\ &= \psi(\mathbf{r}) - \frac{i}{\hbar} \delta\varphi \mathbf{n} \cdot (\mathbf{r} \times \hat{\mathbf{p}}) \psi(\mathbf{r}) = \psi(\mathbf{r}) - \frac{i}{\hbar} \delta\varphi \mathbf{n} \cdot \hat{\mathbf{L}} \psi(\mathbf{r}).\end{aligned}\quad (2.59)$$

Here, $\hat{\mathbf{L}}$ is the angular momentum operator. A rotation by a finite angle φ is expressed as a sum of infinitesimal rotations, giving the equation

$$\tilde{\psi}(\mathbf{r}) = \hat{P}(\varphi, \mathbf{n})\psi(\mathbf{r}) = e^{-i\varphi \mathbf{n} \cdot \hat{\mathbf{L}}/\hbar} \psi(\mathbf{r}). \quad (2.60)$$

The result can be summarized by the following theorem.

Theorem 2 (Rotation of a scalar field). *A transformation of the scalar field $\psi(\mathbf{r})$ to the field $\tilde{\psi}(\mathbf{r})$ with respect to a rotation around the angle φ about the axis $\mathbf{n}$ (with rotation matrix $\underline{\underline{R}}$) is given by*

$$\tilde{\psi}(\mathbf{r}) = \psi(\underline{\underline{R}}^{-1} \cdot \mathbf{r}) = \hat{P}(\varphi, \mathbf{n})\psi(\mathbf{r}), \quad (2.61)$$

with the rotation operator

$$\hat{P}(\varphi, \mathbf{n}) = e^{-i\varphi \mathbf{n} \cdot \hat{\mathbf{L}}/\hbar}$$

Since the angular momentum operator $\hat{\mathbf{L}}$ is Hermitian, it follows that the rotation operator $\hat{P}(\varphi, \mathbf{n})$ is a unitary operator. The components of the angular momentum operator $\hat{L}_x, \hat{L}_y, \hat{L}_z$ are the generators of rotations about the coordinate axes.

2.2.2

Transformation of Vector Fields and Total Angular Momentum

A photon is described by a vector field in terms of a corresponding vector potential $\mathbf{A}(\mathbf{r}, t)$. Vector mesons are particles with rest mass larger than zero described also by vector fields, i.e., transformation of vector fields play a role in classical and quantum theories.

A general vector field $\boldsymbol{\psi}(\mathbf{r})$ is considered in the following. In comparison to the transformation of scalar fields, a rotation of a vector field has to take into account a change of the direction of the vector field itself. The relation similar to (2.57) reads

$$\tilde{\boldsymbol{\psi}}(\mathbf{r}) = \underline{\mathbf{R}} \cdot \boldsymbol{\psi}(\underline{\mathbf{R}}^{-1} \cdot \mathbf{r}). \quad (2.62)$$

Considering an infinitesimal rotation (2.58) $\delta\varphi$ and an expansion up to linear order gives,

$$\begin{aligned} \tilde{\boldsymbol{\psi}}(\mathbf{r}) &= \boldsymbol{\psi}(\underline{\mathbf{R}}^{-1} \cdot \mathbf{r}) + \delta\varphi \mathbf{n} \times \boldsymbol{\psi}(\underline{\mathbf{R}}^{-1} \cdot \mathbf{r}) \\ &= \boldsymbol{\psi}(\mathbf{r} - \delta\varphi \mathbf{n} \times \mathbf{r}) + \delta\varphi \mathbf{n} \times \boldsymbol{\psi}(\mathbf{r}) \\ &= \boldsymbol{\psi}(\mathbf{r}) - \frac{i}{\hbar} \delta\varphi (\mathbf{n} \cdot \hat{\mathbf{L}}) \boldsymbol{\psi}(\mathbf{r}) + \delta\varphi \mathbf{n} \times \boldsymbol{\psi}(\mathbf{r}). \end{aligned} \quad (2.63)$$

The last term of (2.63) can be expressed by means of the skew symmetric matrix $\underline{\mathbf{Z}}$ (cf. (2.22)),

$$\begin{aligned} \mathbf{n} \times \mathbf{r} &= \underline{\mathbf{Z}} \cdot \mathbf{r}, \quad \underline{\mathbf{Z}} = \begin{pmatrix} 0 & -n_z & n_y \\ n_z & 0 & -n_x \\ -n_y & n_x & 0 \end{pmatrix}, \\ \underline{\mathbf{Z}} &= n_x \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} + n_y \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix} + n_z \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\ &= -\frac{i}{\hbar} \left\{ n_x \hat{\mathbf{S}}_x + n_y \hat{\mathbf{S}}_y + n_z \hat{\mathbf{S}}_z \right\} = -\frac{i}{\hbar} \mathbf{n} \cdot \hat{\mathbf{S}}. \end{aligned} \quad (2.64)$$

The spin operator $\hat{\mathbf{S}}$ was introduced in (2.64). Hence, for an infinitesimal rotation of a vector field it follows from (2.63),

$$\begin{aligned} \tilde{\boldsymbol{\psi}}(\mathbf{r}) &= \left\{ 1 - \frac{i}{\hbar} \delta\varphi (\mathbf{n} \cdot \hat{\mathbf{L}}) - \frac{i}{\hbar} \delta\varphi (\mathbf{n} \cdot \hat{\mathbf{S}}) \right\} \boldsymbol{\psi}(\mathbf{r}) \\ &= \left\{ 1 - \frac{i}{\hbar} \delta\varphi (\mathbf{n} \cdot \hat{\mathbf{J}}) \right\} \boldsymbol{\psi}(\mathbf{r}). \end{aligned} \quad (2.65)$$

$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ represents the total angular momentum.³⁾ The result can be generalized to finite angles φ .

3) In a pure classical consideration the operators $\hat{\mathbf{L}}, \hat{\mathbf{S}}, \hat{\mathbf{J}}$ might be defined with $\hbar = 1$.

Theorem 3 (Rotation of a vector field). *A transformation of the vector field $\psi(\mathbf{r})$ to the field $\tilde{\psi}(\mathbf{r})$ with respect to a rotation about the angle φ about the axis $\mathbf{n}$ (with rotation matrix $\underline{\mathbb{R}}$) is given by*

$$\tilde{\psi}(\mathbf{r}) = \underline{\mathbb{R}} \cdot \psi(\underline{\mathbb{R}}^{-1} \cdot \mathbf{r}) = \hat{P}(\varphi, \mathbf{n})\psi(\mathbf{r}), \quad (2.66)$$

$$\hat{P}(\varphi, \mathbf{n}) = e^{-i\varphi \mathbf{n} \cdot \hat{\mathbf{J}}/\hbar}, \quad \hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}. \quad (2.67)$$

The components of the total angular momentum operator $\hat{\mathbf{J}}$ are the generators of rotations around the coordinate axes. The components of $\hat{\mathbf{S}}$ are given by

$$\hat{S}_x = i\hbar \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \hat{S}_y = i\hbar \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix}, \quad \hat{S}_z = i\hbar \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (2.68)$$

The total angular momentum operator $\hat{\mathbf{J}}$ is unitary, because $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ are Hermitian. The Hermiticity of $\hat{\mathbf{S}}$ follows directly from (2.68). Vector fields carry a spin $S = 1$.

2.2.3

Spinors

To investigate the transformation properties of spinors, the transformation of the solution of the PAULI equation

$$-\frac{\hbar}{i} \frac{\partial \psi(\mathbf{r}, t)}{\partial t} = \hat{\mathbf{H}}\psi(\mathbf{r}, t) = \left[\frac{(\hat{\mathbf{p}} - e\mathbf{A})^2}{2m} + V(\mathbf{r}) - \mu_B \underline{\sigma} \cdot \mathbf{B} \right] \psi(\mathbf{r}, t) \quad (2.69)$$

has to be analyzed. Here, $\underline{\sigma} = \mathbf{e}_x \underline{\sigma}_x + \mathbf{e}_y \underline{\sigma}_y + \mathbf{e}_z \underline{\sigma}_z$ is the vector of the PAULI matrices,

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (2.70)$$

As before, the transformation of the spinor $\psi(\mathbf{r})$ is mediated by a unitary operator $\hat{P}(\varphi, \mathbf{n})$,

$$\tilde{\psi}(\mathbf{r}) = \hat{P}(\varphi, \mathbf{n})\psi(\mathbf{r}) \quad (2.71)$$

The unitarity of $\hat{P}$ guarantees that the probability density $\psi^\dagger \psi$ is invariant under coordinate transformations,

$$\tilde{\psi}^\dagger(\mathbf{r})\tilde{\psi}(\mathbf{r}) = (\hat{P}\psi)^\dagger(\hat{P}\psi) = \psi^\dagger \hat{P}^\dagger \hat{P} \psi = \psi^\dagger \psi. \quad (2.72)$$

If a transformation in configuration space of the spinor components is considered, the following relation is assumed to hold,

$$\tilde{\psi}^\dagger(\mathbf{r})\tilde{\psi}(\mathbf{r}) = \psi^\dagger(\underline{\mathbb{R}}^{-1} \cdot \mathbf{r})\psi(\underline{\mathbb{R}}^{-1} \cdot \mathbf{r}). \quad (2.73)$$

The components of a spinor are scalar functions of $\mathbf{r}$ and transform according to Theorem 2. This results in

$$\begin{aligned}\tilde{\psi}^\dagger(\mathbf{r})\tilde{\psi}(\mathbf{r}) &= \left(\hat{P}_L\psi\right)^\dagger \left(\hat{P}_L\psi\right) = \psi^\dagger(\mathbf{r})\hat{P}_L^\dagger\hat{P}_L\psi(\mathbf{r}) \\ \hat{P}_L &= e^{-i\varphi\mathbf{n}\cdot\hat{\mathbf{L}}/\hbar}.\end{aligned}\quad (2.74)$$

Here, $\hat{P}_L$ denotes a transformation of the argument only (cf. Theorem 2). Comparing the general transformation (2.72) and (2.74) leads to the relation

$$\psi^\dagger(\mathbf{r})\hat{P}^\dagger\hat{P}\psi(\mathbf{r}) = \psi^\dagger(\mathbf{r})\hat{P}_L^\dagger\hat{P}_L\psi(\mathbf{r}). \quad (2.75)$$

Hence, $\hat{P}$ consists of two parts. First, the unitary operator $\hat{P}_L$ describes the transformation of the coordinates in the spinor components. The second part $\underline{\mathbf{u}}(\varphi, \mathbf{n})$ is a rotation in spin space ($\mathbb{C}^2$),

$$\hat{P}(\varphi, \mathbf{n}) = \hat{P}_L(\varphi, \mathbf{n})\underline{\mathbf{u}}(\varphi, \mathbf{n}) = \hat{P}_L(\varphi, \mathbf{n})e^{-i\varphi\mathbf{n}\cdot\hat{\mathbf{g}}/2}. \quad (2.76)$$

The concrete form of $\underline{\mathbf{u}}(\varphi, \mathbf{n})$ follows from the transformation properties of the PAULI equation. To guarantee that physical properties calculated from the PAULI equation are invariant under a coordinate system change,

$$\tilde{\psi}^\dagger(\mathbf{r}')\hat{\mathbf{H}}'(\mathbf{r}')\tilde{\psi}(\mathbf{r}') = \psi^\dagger(\mathbf{r})\hat{\mathbf{H}}(\mathbf{r})\psi(\mathbf{r}) \quad (2.77)$$

has to be fulfilled. To determine $\underline{\mathbf{u}}(\varphi, \mathbf{n})$, the spin-dependent part of $\hat{\mathbf{H}}$ has to be investigated. An infinitesimal rotation leads to (cf. [41], p. 46ff for details)

$$\underline{\mathbf{u}}(\varphi, \mathbf{n}) = e^{-i\varphi\mathbf{n}\cdot\hat{\mathbf{g}}/2}. \quad (2.78)$$

Expanding equation (2.78) in terms of a TAYLOR series, restricting the calculation to $|\mathbf{n}| = 1$, and keeping in mind the algebra of the PAULI matrices,⁴⁾ it is possible to reformulate $\underline{\mathbf{u}}$ as,

$$\underline{\mathbf{u}}(\varphi, \mathbf{n}) = \begin{pmatrix} \cos \frac{\varphi}{2} - in_z \sin \frac{\varphi}{2} & -(n_y + in_x) \sin \frac{\varphi}{2} \\ (n_y - in_x) \sin \frac{\varphi}{2} & \cos \frac{\varphi}{2} + in_z \sin \frac{\varphi}{2} \end{pmatrix}. \quad (2.80)$$

Matrices like in equation (2.80) are elements of the group of 2-dimensional unitary matrices with determinant 1, called $SU(2)$. As will be discussed in Section 8.2, there is a 2-to-1 mapping between the rotations in spin space and the rotations in real space. That means, vice versa, to each rotation in real space $\underline{\mathbf{R}}$, there correspond two matrices in spin space that differ from each other by a minus sign, $\underline{\mathbf{u}}(\underline{\mathbf{R}})$ and $-\underline{\mathbf{u}}(\underline{\mathbf{R}})$. Within GTPack it is possible to evaluate (2.80) for a certain angle and rotation axis using the command **GTSU2Matrix**. However, the matrix $-\underline{\mathbf{u}}$ is revealed as a standard. An example for a rotation with an angle $\frac{2}{3}\pi$ about the z -axis is shown in Figure 2.10.

4) The PAULI matrices fulfill the following multiplication rules,

$$\underline{\underline{\sigma}}_i \cdot \underline{\underline{\sigma}}_j = \delta_{i,j}\underline{\underline{1}} + i\epsilon_{ijk}\underline{\underline{\sigma}}_k. \quad (2.79)$$

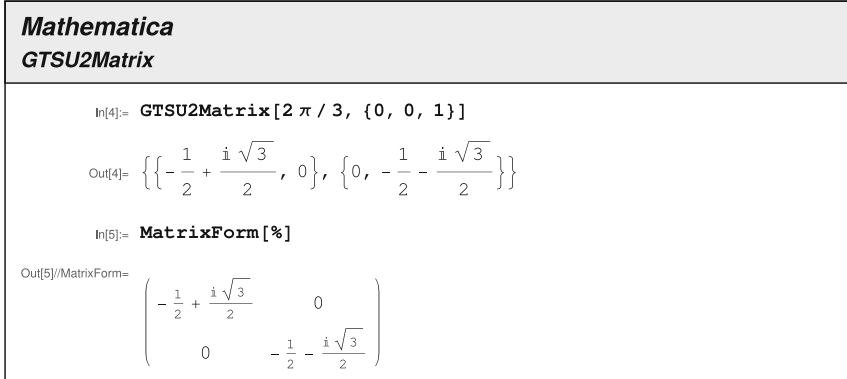


Figure 2.10 Calculation of a rotation matrix in spin-space with the help of **GTSU2Matrix**.

Analogously to equation (2.14), rotation matrices in spin-space can be evaluated from three EULER angles. Using the zyz -convention and calculating the related matrices according to equation (2.80), the following rotation matrix can be obtained,

$$\begin{aligned}
 \underline{\underline{U}}(\alpha, \beta, \gamma) &= \\
 &= \begin{pmatrix} e^{-\frac{i}{2}\alpha} & 0 \\ 0 & e^{\frac{i}{2}\alpha} \end{pmatrix} \begin{pmatrix} \cos \frac{\beta}{2} & -\sin \frac{\beta}{2} \\ \sin \frac{\beta}{2} & \cos \frac{\beta}{2} \end{pmatrix} \begin{pmatrix} e^{-\frac{i}{2}\gamma} & 0 \\ 0 & e^{\frac{i}{2}\gamma} \end{pmatrix} \\
 &= \begin{pmatrix} e^{-\frac{i}{2}(\alpha+\gamma)} \cos \frac{\beta}{2} & -e^{-\frac{i}{2}(\alpha-\gamma)} \sin \frac{\beta}{2} \\ e^{\frac{i}{2}(\alpha-\gamma)} \sin \frac{\beta}{2} & e^{\frac{i}{2}(\alpha+\gamma)} \cos \frac{\beta}{2} \end{pmatrix}. \tag{2.81}
 \end{aligned}$$

The above equation can be evaluated using **GTGetSU2Matrix**. In contrast to **GT-SU2Matrix**, which is designed analogously to the *Mathematica* command **RotationMatrix**, **GTGetSU2Matrix** is capable of transforming matrices, quaternions, symbols, or EULER angles into a rotation matrix in spin-space. The usage of **GTGetSU2Matrix** is demonstrated in Figure 2.11.

To construct improper rotations in spin-space, a representation for the inversion operator needs to be established. Historically, two different matrices were suggested, denoted as the PAULI gauge and the CARTAN gauge (cf. [38, p. 106, p. 194]). Since the angular momentum is an axial vector, which is invariant under inversion, PAULI argued that also the spin has to be invariant under inversion. Therefore, the matrix representation of the inversion in the PAULI gauge is given by the identity matrix,

$$\underline{\underline{U}}^{\text{Pauli}}(\hat{I}) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{2.82}$$

For rotations in three-dimensional space defined by a rotation matrix $\underline{\underline{R}}$, proper rotations have a positive determinant $\det \underline{\underline{R}} = 1$, whereas improper rotations have

Mathematica

GTGetSU2Matrix

SU(2) matrix from Euler angles

$$\text{In[9]:= GTGetSU2Matrix}\left[\left\{\left\{0, 0, \frac{2\pi}{3}\right\}, 1\right\}\right]$$

$$\text{Out[9]= } \left\{\left\{-\frac{1}{2} + \frac{i\sqrt{3}}{2}, 0\right\}, \left\{0, -\frac{1}{2} - \frac{i\sqrt{3}}{2}\right\}\right\}$$

SU(2) matrix from quaternion

$$\text{In[10]:= GTGetSU2Matrix}\left[\left\{\frac{1}{2}, \left\{0, 0, \frac{\sqrt{3}}{2}\right\}\right\}\right]$$

$$\text{Out[10]= } \left\{\left\{-\frac{1}{2} + \frac{i\sqrt{3}}{2}, 0\right\}, \left\{0, -\frac{1}{2} - \frac{i\sqrt{3}}{2}\right\}\right\}$$

SU(2) matrix from symbol

$$\text{In[11]:= GTGetSU2Matrix}[C3z]$$

$$\text{Out[11]= } \left\{\left\{-\frac{1}{2} + \frac{i\sqrt{3}}{2}, 0\right\}, \left\{0, -\frac{1}{2} - \frac{i\sqrt{3}}{2}\right\}\right\}$$

Figure 2.11 SU(2) matrices can be obtained from EULER angles, quaternions, or symbols of symmetry elements with the help of **GTGetSU2Matrix**. The symbol C_{3z} denotes a counter-clockwise rotation by $\frac{2}{3}\pi$ about the z-axis.

a negative determinant $\det \underline{\mathbf{R}} = -1$. It can be seen that this behavior is not reflected by the PAULI gauge for rotation matrices in spin-space. A second possibility with a negative determinant is given by the CARTAN gauge, where the inversion matrix is represented by

$$\underline{\mathbf{u}}^{\text{Cartan}}(\hat{I}) = \begin{pmatrix} -i & 0 \\ 0 & -i \end{pmatrix}. \quad (2.83)$$

Within GTPack the PAULI gauge is used. The results of this section are summarized in the following theorem.

Theorem 4 (Rotation of a spinor field). *A transformation of the spinor field $\psi(\mathbf{r})$ to the field $\tilde{\psi}(\mathbf{r})$ with respect to a rotation around the angle φ about the axis $\mathbf{n}$ (with rotation matrix $\underline{\mathbf{R}}$ and spin-rotation matrix $\underline{\mathbf{u}}$) is given by*

$$\tilde{\psi}(\mathbf{r}) = \underline{\mathbf{u}} \cdot \psi(\underline{\mathbf{R}}^{-1} \cdot \mathbf{r}) = \hat{P}(\varphi, \mathbf{n})\psi(\mathbf{r}), \quad (2.84)$$

$$\hat{P}(\varphi, \mathbf{n}) = e^{-i\varphi \mathbf{n} \cdot \hat{\mathbf{J}}/\hbar}, \quad \hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{s}}. \quad (2.85)$$

The components of the total angular momentum operator are the generators of rotations around the coordinate axes. The components of the spin vector $\mathbf{s}$ are given

by

$$\hat{s}_x = \frac{\hbar}{2} \underline{\sigma}_x, \quad \hat{s}_y = \frac{\hbar}{2} \underline{\sigma}_y, \quad \hat{s}_z = \frac{\hbar}{2} \underline{\sigma}_z. \quad (2.86)$$

Task 5 (Rotation in spin-space). Derive equation (2.80) from equation (2.78). Try to use *Mathematica* and the commands **PauliMatrix** and **MatrixPower**.

3

Basics Abstract Group Theory

Il suffit, pour cela, de choisir une fonction symétrique des diverses valeurs que prend, par toutes les permutations de l'un des groupes partiels, une fonction qui n'est invariable pour aucune substitution.

Évariste Galois

(Journal de mathématiques pures et appliquées, 11, 417–444, (1846))

The chapter provides the definition of a group as well as related algebraic structures. Groups itself can be classified by their order as finite and infinite groups. Additionally, infinite groups can be discrete or continuous. Within this book, the focus is on crystallographic point groups which are finite and space groups which are discrete infinite groups. Groups itself are sets and contain subsets of special relevance, such as classes of mutually equivalent elements, subgroups and cosets. Such structures help classifying specific groups and also provide physically relevant information as will be important later. Maps between groups, especially structure preserving maps are an important concept which will be introduced during this chapter. Among others, it introduces the notion of similar groups and provides the basic framework for representation theory.

3.1

Basic Definitions

Installation of groups and basic group properties	
GTInstallGroup	Installation of point and space groups
GTGenerators	Determines the generators of a group
GTGroupFromGenerators	Installs a group from a set of generators
GTTableToGroup	Constructs a matrix representation from a given multiplication table

GTMultTable	Calculates the multiplication table of a group
GTGroupOrder	Estimates the order of a group
GTOrderOfElement	Estimates the order of a symmetry element
GTGetSubGroups	Finds subgroups of a group
GTGroupQ	Tests if a list of elements is a group
GTSubGroupQ	Tests if $\mathcal{G}'$ is a subgroup of $\mathcal{G}$
GTAbelianQ	Tests if a group is Abelian

Groups are sets of distinct elements together with an operation called ‘multiplication.’ In applications of group theory to problems of solid-state physics the elements represent the symmetries of crystals or atomic clusters, i.e., they are given by translations and rotations that transform these objects into itself.

Definition 4 (Group). *A set $\mathcal{G}$ together with an operation (called multiplication) is called a group, if the following conditions are satisfied.*

- If $a, b \in \mathcal{G}$, then also the product $c = a \circ b$ is a member of the group, i.e., $c \in \mathcal{G}$.*
- The associative law holds, i.e., if $a, b, c \in \mathcal{G}$ then $a \circ (b \circ c) = (a \circ b) \circ c$.*
- There exists an identity element $E \in \mathcal{G}$ with the property $E \circ a = a \circ E = a$ for all $a \in \mathcal{G}$.*
- For each element $a \in \mathcal{G}$ there is an inverse element $a^{-1} \in \mathcal{G}$ such that $a \circ a^{-1} = a^{-1} \circ a = E$.*

The following example will show the installation of groups within GTPack.

Example 4 (Installation of point groups in GTPack). Point groups denote the finite crystallographic groups that represent the local symmetry of an atom (point) within a crystal. In the 3-dimensional space 32 point groups can be defined. Within GTPack they can be installed using the command **GTInstallGroup**. Figure 3.1 shows an example for the point group C_{4v} , which contains all planar symmetries that leave a square invariant. After installing the group, **GTGroupQ** is applied to check if the four conditions of Definition 4 are satisfied.

Groups containing a finite number of elements are called *finite groups*. Crystallographic point groups are typical examples of finite groups. An *infinite group* contains an infinite number of elements. Examples are the translational group of a crystal which is infinite, but discrete. All 3×3 real orthogonal matrices, related to rotations in three-dimensional Euclidean space, form an infinite continuous group.

Definition 5 (Continuous Group). *A group $\mathcal{G}$ whose elements $g = g(\alpha_1, \alpha_2, \dots, \alpha_r)$ depend continuously on the independent parameters $\alpha_1, \alpha_2, \dots, \alpha_r$ is called a continuous group. The number r of independent parameters is called the dimension of the group.*

Mathematica**GTInstallGroup, GTGroupQ**

Installation of a point group using GTInstallGroup.

```
In[8]:= c4v = GTInstallGroup[C4v]
```

The standard representation has changed to $O(3)$

```
Out[8]:= {Ee, C2z, C4z^-1, C4z, IC2x, IC2a, IC2b, IC2y}
```

To check if a set of elements forms a group, GTGroupQ can be used.

```
In[9]:= GTGroupQ[c4v]
```

```
Out[9]:= True
```

The group conditions can also be verified manually.

```
In[10]:= C2z ◦ (C4z ◦ IC2x) == (C2z ◦ C4z) ◦ IC2x
```

```
Out[10]:= True
```

```
In[11]:= IC2a ◦ Ee == Ee ◦ IC2a == IC2a
```

```
Out[11]:= True
```

```
In[12]:= C4z ◦ C4zi
```

```
Out[12]:= Ee
```

Figure 3.1 Installation of the point group C_{4v} . To verify that C_{4v} forms a group GTGroupQ is applied. In a second step, the group conditions are checked manually.¹⁾

According to this definition, a 3×3 matrix as a representation of a rotation, will be parameterized by the three Euler angles. *Lie groups* are special continuous groups, where the elements are differentiable functions of the parameters. The continuous groups will play a minor role throughout this book. Special properties of such groups are mentioned if necessary.

In the following, some minor definitions are given. The *order of the group* – $\text{ord}(\mathcal{G})$ denotes the number of elements of a finite group (GTGroupOrder). Commutativity is not a basic property of the multiplication (Definition 4). However, in cases where $a \circ b = b \circ a \ \forall a, b \in \mathcal{G}$ holds, the group is called *Abelian* (GTAbelianQ). The properties of a group can be depicted in form of a *multiplication table*, where the result of the multiplication of all possible combinations of group elements is presented. In Figure 3.2, the multiplication table of the point group C_{4v} is shown (GTMultTable). The multiplication table of an Abelian group is symmetric. As can be verified, this is not the case for C_{4v} ($IC_{2a} \circ IC_{2y} \neq IC_{2y} \circ IC_{2a}$).

Per definition, a group is closed under its multiplication. For finite groups it follows that a finite number of multiplications p of a group element a with itself leads to the identity element E , $a^p = E$. The smallest natural number p is called the *order of the element* $p = \text{ord}(a)$ (GTOrderOfElement).

1) In *Mathematica* the symbol $\circ$ is obtained by \[SmallCircle] or ESC sc ESC. You will find it also on the GTPack palette.

Mathematica**GTMultTable, GTAbelianQ**

```
In[8]:= GTMultTable[c4v];
```

	Ee	C _{2z}	C _{4z} ¹	C _{4z}	IC _{2x}	IC _{2a}	IC _{2b}	IC _{2y}
Ee	Ee	C _{2z}	C _{4z} ¹	C _{4z}	IC _{2x}	IC _{2a}	IC _{2b}	IC _{2y}
C _{2z}	C _{2z}	Ee	C _{4z}	C _{4z} ¹	IC _{2y}	IC _{2b}	IC _{2a}	IC _{2x}
C _{4z} ¹	C _{4z} ¹	C _{4z}	C _{2z}	Ee	IC _{2b}	IC _{2x}	IC _{2y}	IC _{2a}
C _{4z}	C _{4z}	C _{4z} ¹	Ee	C _{2z}	IC _{2a}	IC _{2y}	IC _{2x}	IC _{2b}
IC _{2x}	IC _{2x}	IC _{2y}	IC _{2a}	IC _{2b}	Ee	C _{4z} ¹	C _{4z}	C _{2z}
IC _{2a}	IC _{2a}	IC _{2b}	IC _{2y}	IC _{2x}	C _{4z}	Ee	C _{2z}	C _{4z} ¹
IC _{2b}	IC _{2b}	IC _{2a}	IC _{2x}	IC _{2y}	C _{4z} ¹	C _{2z}	Ee	C _{4z}
IC _{2y}	IC _{2y}	IC _{2x}	IC _{2b}	IC _{2a}	C _{2z}	C _{4z}	C _{4z} ¹	Ee

```
In[9]:= GTAbelianQ[c4v]
```

```
Out[9]:= False
```

Figure 3.2 Multiplication table of the non-Abelian point group C_{4v} calculated using GTMultTable.

Theorem 5 (Fermat's theorem). *For every element $a \in G$ and $g = \text{ord}(G)$ the relation $a^g = E$ holds.*

A set of group elements of G is called the *generators* of G , if all group elements can be found by a finite number of multiplications of the generators. The minimal number of generators is called the *basis of the group*. The *rank of the basis* is the number of generators in the basis. The choice of the basis is not unique. GTPack offers commands to find the generators of a group or to construct the group from a set of generators (GTGenerators, GTGroupFromGenerators). A group is called *cyclic group* (GTCyclicQ), if it can be generated from one element only. An example of the application of GTGenerators and GTGroupFromGenerators is shown in Figure 3.3.

Task 6 (Generators of a group). Install the point group D_{4h} . Demonstrate that the choice of generators is not unique. Find three different sets of generators.

A subset $G' \subset G$ that satisfies the definition of a group is called a *subgroup* of G . The subsets $\{E\}$ and G are trivial subgroups of G . Within GTPack, subgroups of a group can be found using GTGetSubGroups (see Example 3.6). A test of the relation $G' \subset G$ can be performed with GTSubGroupQ.

Theorem 6 (Lagrange's theorem). *If G' is a subgroup of G ($G' \subset G$) then its order g' is a factor of the order $g = \text{ord}(G)$ of G . The integer g/g' is called the *index* of G' in G .*

Example 5 (Installation of a group from its multiplication table). Alternatively to GTInstallGroup, GTTableToGroup can be used to install a finite group from its mul-

Mathematica**GTGenerators, GTGroupFromGenerators**

The elements of the group C_{4v} .

In[15]:= **c4v**

Out[15]= $\{Ee, C_{2z}, C_{4z}^{-1}, C_{4z}, IC_{2x}, IC_{2a}, IC_{2b}, IC_{2y}\}$

The group has two generators.

In[16]:= **generators = GTGenerators[c4v]**

Out[16]= $\{IC_{2a}, C_{4z}\}$

Using the generators to install the group, the same set of elements as before is obtained.

In[17]:= **GTGroupFromGenerators[generators]**

Out[17]= $\{Ee, C_{2z}, C_{4z}^{-1}, C_{4z}, IC_{2x}, IC_{2a}, IC_{2b}, IC_{2y}\}$

Figure 3.3 Calculating the generators of the group C_{4v} using **GTGenerators**. The group was installed in Figure 3.1.

Mathematica**GTableToGroup**

Defining the multiplication table of Klein's four - group.

In[11]:= **FourGroup = {{1, a, b, ab}, {a, 1, ab, b}, {b, ab, 1, a}, {ab, b, a, 1}};**

Installing the group using **GTableToGroup**.

In[12]:= **fgr = GTableToGroup[{1, a, b, ab}, FourGroup, GVerbose → False];**

A calculation of the multiplication table from the installed group elements gives the expected result.

In[13]:= **GTableToGroup[fgr];**

	1	a	b	ab
1	1	a	b	ab
a	a	1	ab	b
b	b	ab	1	a
ab	ab	b	a	1

The installed symbols can be used in the following.

In[14]:= **a ° ab**

Out[14]= **b**

Figure 3.4 Installation of KLEIN's four group from the multiplication table.

tiplication table within **GTPack**. This approach is especially useful if a group is not implemented within **GTPack**. As an example, the **KLEIN** four group is considered. With four elements, it represents the smallest noncyclic group. An example of the application of **GTableToGroup** to the **KLEIN** four group is shown in Figure 3.4. By

applying **GTTableToGroup**, the group elements are represented by permutation matrices. The defined symbols of the elements can be used afterwards within the **GPack** commands.

Task 7 (Properties of groups). A set $\{E, C_{2x}, C_{2y}, C_{2z}\}$ is given. Proof that the set forms a group. Is the group Abelian? Proof that the multiplication table of this group has the same structure as the multiplication table of the KLEIN four group.

3.1.1

Isomorphism and Homomorphism

A group is well defined by its inner structure, which is independent of the nature of the elements (matrices, operators, permutations, ...) or the kind of group multiplication. The investigation of mappings between groups allows one to study their relationship, differences, or similarity.

Definition 6 (Homomorphism). A mapping $f : \mathcal{G} \rightarrow \mathcal{G}'$ of a group $(\mathcal{G}, \bullet)$ to a group $(\mathcal{G}', \circ)$ is called homomorphism if

$$f(a_1 \bullet a_2) = f(a_1) \circ f(a_2), \quad \text{for all } a_1, a_2 \in \mathcal{G}. \quad (3.1)$$

The set of elements of $\mathcal{G}$ mapped to $E' \in \mathcal{G}'$ (the identity of $\mathcal{G}'$) is called the kernel $\mathcal{N}_K$ of the homomorphism.

If $\mathcal{U}$ is a subgroup of $\mathcal{G}$ ($\mathcal{U} \subset \mathcal{G}$) and $f : \mathcal{G} \rightarrow \mathcal{G}'$ is a homomorphism, then $\mathcal{U}'$ is also a subgroup of $\mathcal{G}'$. A homomorphic mapping of a group $\mathcal{G}$ to one of its subgroups $\mathcal{U} \subset \mathcal{G}$ is called *endomorphism*.

Definition 7 (Isomorphism). A bijective homomorphism $f : \mathcal{G} \rightarrow \mathcal{G}'$ is called isomorphism, $\mathcal{G} \cong \mathcal{G}'$. If $\mathcal{G} \equiv \mathcal{G}'$, the homomorphism is called *automorphism*.

Example 6 (Subgroups of C_{4v}). The multiplication table of C_{4v} is given in Figure 3.2. It can be concluded that the set of elements $C_4 = \{E, C_{4z}, C_{4z}^{-1}, C_{2z}\}$ is a subgroup of C_{4v} , $C_4 \subset C_{4v}$. Other subgroups of C_{4v} are $C_2 = \{E, C_{2z}\}$ and $C_s = \{E, IC_{2y}\}$. Since they have a similar multiplication table, C_s and C_2 are isomorphic, $C_s \cong C_2$. An endomorphic mapping $f : C_{4v} \rightarrow C_s$ is given by

$$f : \{E, C_{4z}, C_{4z}^{-1}, C_{2z}\} \rightarrow E, \quad \{IC_{2x}, IC_{2y}, IC_{2a}, IC_{2b}\} \rightarrow IC_{2y}. \quad (3.2)$$

The subgroups can be found with **GTGetSubGroups**. The relationships can be checked by means of **GTSUBGROUPQ**.

3.2

Structure of Groups

Structure of groups	
GTConjugateElement	Finds the conjugate element
GTClasses	Constructs the classes of a group
GTClassMult	Gives class multiplication coefficients
GTClassMultTable	Calculates the class multiplication table
GTCenter	Finds the center of the group
GTLeftCosets	Calculates left cosets of $\mathcal{G}$ with respect to $\mathcal{U} \subset \mathcal{G}$
GTRightCosets	Calculates right cosets of $\mathcal{G}$ with respect to $\mathcal{U} \subset \mathcal{G}$
GTNormalizer	Calculates the normalizer of $\mathcal{G}'$ with respect to a supergroup $\mathcal{G}$
GTConjugacyClass	Constructs conjugacy classes for $\mathcal{G}' \subset \mathcal{G}$
GTInvSubGroups	Gives all normal divisors of $\mathcal{G}$
GTInvSubGroupQ	Gives true, if $\mathcal{U} \subset \mathcal{G}$ is a normal divisor of $\mathcal{G}$

Equivalence relations are important to classify elements of a given set $\mathcal{M}$. One can think of assigning a specific property (e.g., “length” or “color”) to every element of $\mathcal{M}$. The element a is said to be equivalent to b ($a \sim b$), if the elements share this property.

Definition 8 (Equivalence relation). *A relation $\sim$ on a set $\mathcal{M}$ is called the equivalence relation if the following conditions are satisfied for all elements $a, b, c \in \mathcal{M}$*

1. *reflexivity: $a \sim a$*
2. *symmetry: if $a \sim b$ then also $b \sim a$*
3. *transitivity: if $a \sim b$ and $b \sim c$, then also $a \sim c$*

By means of an equivalence relation a set $\mathcal{M}$ is subdivided into subsets called *classes* or *equivalence classes*. An equivalence class $\llbracket a \rrbracket$ of $a \in \mathcal{M}$ contains all elements $a_i \in \mathcal{M}$, which are equivalent to a :

$$\llbracket a \rrbracket := \{a_i \mid a_i \in \mathcal{M} \wedge a \in \mathcal{M} \wedge a_i \sim a\} . \quad (3.3)$$

Because of transitivity of the equivalence relation, every element of the equivalence class may be used as a representant,

$$a \sim b \Rightarrow \llbracket a \rrbracket = \llbracket b \rrbracket . \quad (3.4)$$

All equivalence classes are disjoint,

$$a \not\sim b \Rightarrow \llbracket a \rrbracket \cap \llbracket b \rrbracket = \emptyset . \quad (3.5)$$

The set $\mathcal{M}$ can be obtained by a set sum of all inequivalent equivalence classes,

$$\mathcal{M} = \sum_i \llbracket a_i \rrbracket, \quad \llbracket a_i \rrbracket \cap \llbracket a_j \rrbracket = \emptyset, \quad a_i \sim a_j. \quad (3.6)$$

3.2.1

Classes

A valid equivalence relation of a group is given by the so-called conjugation operation.

Definition 9 (Conjugate element). *An element $a \in \mathcal{G}$ is said to be the conjugate element of an element $b \in \mathcal{G}$ if there exists an element $c \in \mathcal{G}$ such that*

$$a = c \circ b \circ c^{-1}. \quad (3.7)$$

The equivalence relation in terms of conjugate elements will be important throughout the book. If not stated otherwise, the term classes will be used in this connection.

Definition 10 (Classes). *A class is a complete set of conjugate elements:*

$$C_a = \{a_i \mid a, b \in \mathcal{G} \wedge a_i = b \circ a \circ b^{-1} \wedge a \text{ fixed}\}. \quad (3.8)$$

The associated commands for deriving conjugate elements and classes in GTPack are **GTConjugateElement** and **GTClasses**. Classes exhibit the following properties.

Theorem 7 (Classes of groups). *For a group $\mathcal{G}$ the following statements about classes hold.*

1. *Every element of $\mathcal{G}$ belongs to exactly one class of $\mathcal{G}$, i.e., an element of $\mathcal{G}$ cannot be a member of two different classes.*
2. *The identity element E forms a class on its own.*
3. *In an Abelian group each element forms a class on its own.*
4. *A class contains only elements of the same order.*

Proof. The conjugation is an equivalence relation. Thus, symmetry and transitivity lead to the fact that classes are disjoint subsets of a group. That the identity E forms a class on its own follows from

$$c \circ E \circ c^{-1} = c \circ c^{-1} = E. \quad (3.9)$$

Similarly, for Abelian groups, where the multiplication is commutative, it follows

$$c \circ b \circ c^{-1} = c \circ c^{-1} \circ b = b. \quad (3.10)$$

The last consequence follows from the fact that if $a \sim b$ then also $a^k \sim b^k$. Assuming $a = c \circ b \circ c^{-1}$, this can be verified via,

$$a^k = (c \circ b \circ c^{-1})^k = (c \circ b \circ c^{-1}) \circ (c \circ b \circ c^{-1}) \circ \dots = c \circ b^k \circ c^{-1}. \quad (3.11)$$

Thus, if $\text{ord}(a) = n$ all elements of the class have order n . $\square$

A special subgroup of a group $\mathcal{G}$ is given by the set of all self-adjoint elements.

Definition 11 (Center). *An element of $\mathcal{G}$ that commutes with all elements of the group $a = z_i \circ a \circ z_i^{-1} \forall z_i \in \mathcal{G}$ is said to be self-adjoint. The set of all self-adjoint elements forms a subgroup, called the center of the group.*

Within GTPack the center of a group can be obtained using **GTCenter**. An example for the group C_{4v} is shown in Example 7.

Definition 12 (Class multiplication). *The multiplication of two classes is given by the multiplication of all elements of the first class with all elements of the second class, by taking into account the order of the operation,*

$$K_i \cdot K_j = \sum_{l=1}^r h_{ij,l} K_l. \quad (3.12)$$

The coefficients $h_{ij,l}$ are called class-multiplication coefficients. The result of class multiplication consists of complete classes.

An example for class multiplication within GTPack is presented in Example 7.

In connection to the term subgroup, the group $\mathcal{G}$ is called the *supergroup* or *covering group* of $\mathcal{G}'$ if $\mathcal{G} \supset \mathcal{G}'$.

Definition 13 (Normalizer). *The normalizer $\mathcal{N}$ of a group $\mathcal{U}$ with respect to one of its supergroups $\mathcal{G}$ is the set of elements $g \in \mathcal{G}$ mapping $\mathcal{U}$ onto itself.*

$$\mathcal{N}(\mathcal{U}|\mathcal{G}) := \{g \in \mathcal{G} \mid g \mathcal{U} g^{-1} = \mathcal{U}\}. \quad (3.13)$$

The group $\mathcal{U}$ is a subgroup of the normalizer and its covering group $\mathcal{U} \subseteq \mathcal{N}(\mathcal{U}|\mathcal{G}) \subseteq \mathcal{G}$. **GTNormalizer** calculates the normalizer of a group with respect to its covering group (cf. Figure 3.6). Another structure, based on the definition of conjugate elements is the so-called *conjugacy class* of a subgroup.

Definition 14 (Conjugated subgroups). *Let $\mathcal{U}$ be a subgroup of $\mathcal{G}$ ($\mathcal{U} \subset \mathcal{G}$). The set of all subgroups conjugated to $\mathcal{U}$ is given by*

$$[\mathcal{U}]_{\mathcal{G}} := \{g \mathcal{U} g^{-1}, g \in \mathcal{G}\}. \quad (3.14)$$

Conjugated subgroups are isomorphic to $\mathcal{U}$.

The concept of conjugated subgroups will be used, e.g., in the discussion of site-symmetry in Section 4.2.3.

Example 7 (Classes and class multiplication in C_{4v}). Figure 3.5 shows how to calculate the center, the classes, and the class multiplication table for the point group C_{4v} by means of the GTPack commands **GTCenter**, **GTClasses**, and **GTClassMultTable**. C_{4v} was introduced in Example 4. It has five classes $\{E\}$, $\{C_{2z}\}$, $\{IC_{2x}, IC_{2y}\}$, $\{IC_{2a}, IC_{2b}\}$, and $\{C_{4z}, C_{4z}^{-1}\}$. The center is given by $\{E, C_{2z}\}$.

Mathematica**GTCenter, GTClasses, GTClassMultTable**

In[8]:= **c4v = GTInstallGroup[C4v]**

The standard representation has changed to $O(3)$

Out[8]:= $\{Ee, C_{2z}, C_{4z}^{-1}, C_{4z}, IC_{2x}, IC_{2a}, IC_{2b}, IC_{2y}\}$

The center of the group C_{4v} consists of two elements.

In[9]:= **GTCenter[c4v]**

Out[9]:= $\{Ee, C_{2z}\}$

C_{4v} has 5 conjugacy classes.

In[10]:= **cls = GTClasses[c4v]**

Out[10]:= $\{\{Ee\}, \{IC_{2x}, IC_{2y}\}, \{IC_{2a}, IC_{2b}\}, \{C_{4z}^{-1}, C_{4z}\}, \{C_{2z}\}\}$

The class multiplication table can be calculated with GTClassMultTable.

In[11]:= **GTClassMultTable[cls];**

C1 = $\{Ee\}$

C2 = $\{IC_{2x}, IC_{2y}\}$

C3 = $\{IC_{2a}, IC_{2b}\}$

C4 = $\{C_{4z}^{-1}, C_{4z}\}$

C5 = $\{C_{2z}\}$

	C1	C2	C3	C4	C5
C1	C1	C2	C3	C4	C5
C2	C2	2 C1 + 2 C5	2 C4	2 C3	C2
C3	C3	2 C4	2 C1 + 2 C5	2 C2	C3
C4	C4	2 C3	2 C2	2 C1 + 2 C5	C4
C5	C5	C2	C3	C4	C1

Figure 3.5 The application of GTCenter, GTClasses, and GTClassMultTable for calculating the center, the classes, and the class multiplication table of the point group C_{4v} .

Example 8 (Calculating the normalizer within GTPack). Figure 3.6 illustrates how to calculate the normalizer of the group C_5 with respect to the covering group D_{3h} . In total, D_{3h} exhibits 14 subgroups, as can be checked with **GTGetSubGroups**. One of the subgroups is the group $C_5 = \{Ee, IC_{2y}\}$. The normalizer $\mathcal{N}(C_5|D_{3h})$ is given by the group $C_{2v} = \{Ee, C_{2x}, IC_{2y}, IC_{2z}\}$.

3.2.2

Cosets and Normal Divisors

With respect to a particular subgroup, a group can be subdivided into left and right cosets. Elements within a coset can be regarded as equivalent in terms of an equivalence relation.

Mathematica**GTGetSubGroups,GTNormalizer**

Install the group D_{3h} .

```
In[8]:= d3h = GTInstallGroup[D3h]
```

The standard representation has changed to $O(3)$

```
Out[8]= {Ee, C2B, C2A, C2X, C3z^-1, C3z, IC2D, IC2C, IC2Y, IC2z, IC6z, IC6z^-1}
```

The subgroups of D_{3h} are given by

```
In[9]:= d3hsub = GTGetSubGroups[d3h]
```

```
sg = d3hsub[[6]];
```

```
Out[9]= {{C2A, Ee}, {C2B, Ee}, {C2X, Ee}, {Ee, IC2C}, {Ee, IC2D},
          {Ee, IC2Y}, {Ee, IC2z}, {C3z, C3z^-1, Ee}, {C2A, Ee, IC2C, IC2z},
          {C2B, Ee, IC2D, IC2z}, {C2X, Ee, IC2Y, IC2z}, {C2A, C2B, C2X, C3z, C3z^-1, Ee},
          {C3z, C3z^-1, Ee, IC2C, IC2D, IC2Y}, {C3z, C3z^-1, Ee, IC2z, IC6z, IC6z^-1}}
```

For example, the group D_{3h} is the covering group of the group $C_s = \{Ee, IC_{2Y}\}$.

The respective normalizer is the group C_{2v} .

```
In[11]:= norm = GTNormalizer[d3h, sg]
```

```
Out[11]= {Ee, C2X, IC2Y, IC2z}
```

Figure 3.6 Calculating the normalizer of C_s with respect to the covering group D_{3h} .

Definition 15 (Cosets). $\mathcal{U}$ is a subgroup of $\mathcal{G}$ ($\mathcal{U} \subseteq \mathcal{G}$). The following subsets of $\mathcal{G}$ are denoted as left cosets $a\mathcal{U}$ and right cosets $\mathcal{U}a$, respectively,

$$a\mathcal{U} = \{a \circ p \mid p \in \mathcal{U} \subseteq \mathcal{G}\}, \quad a \in \mathcal{G}, \quad (3.15)$$

$$\mathcal{U}a = \{p \circ a \mid p \in \mathcal{U} \subseteq \mathcal{G}\}, \quad a \in \mathcal{G} \quad (3.16)$$

In general, the left and right cosets with respect to a particular element $a \in \mathcal{G}$ do not necessarily contain the same elements. However, the following theorems hold for both, left and right cosets. They will be given without proof.

Theorem 8 (Theorems on left and right cosets). Let $\mathcal{U} \subset \mathcal{G}$ be a subgroup of $\mathcal{G}$. Then, the following statements on left and right cosets hold.

1. For $a \in \mathcal{U}$, it follows $a\mathcal{U} = \mathcal{U}a = \mathcal{U}$.
2. For $a \notin \mathcal{U}$, $a\mathcal{U}$ and $\mathcal{U}a$ do not form a group.
3. Every element of $\mathcal{G}$ belongs to exactly one left (right) coset, i.e., two cosets are either identical or disjoint.
4. Every coset has the same number of elements $n = \text{ord}(\mathcal{U})$.
5. Is $b \in a\mathcal{U}$ then $b\mathcal{U}$ is identical to $a\mathcal{U}$. Every element of the coset can be used as a representant of the coset.
6. The number of left (right) cosets of $\mathcal{U}$ in $\mathcal{G}$ is called index and denoted by $\text{ind}(\mathcal{U})$. The index is given by $\text{ind}(\mathcal{U}) = \text{ord}(\mathcal{G}) / \text{ord}(\mathcal{U})$.

Task 8 (Theorems on cosets). Install the point group O . Proof that the group D_4 is a proper subgroup. Show, using D_4 as the subgroup, that all statements in Theorem 8 are correct.

By taking into account all elements of a group G for the decomposition into left (right) cosets, the set G is subdivided into disjoint sets. A special case is given if the decomposition into left cosets is equal to the decomposition into right cosets.

Definition 16 (Invariant subgroup). A subgroup $S \subset G$ is called invariant subgroup $S \triangleleft G$ (normal subgroup, normal divisor) if $x \circ S \circ x^{-1} = S$ for all $x \in G$. In other words, the right and the left cosets of an invariant subgroup S of the group G are identical.

Theorem 9 (Classes and invariant subgroups). A subgroup $S \in G$ forms an invariant subgroup if and only if S consists of complete classes of G .

Proof. $\Rightarrow$: If S consists of complete classes of G it follows that next to $s \in S$ also $g \circ s \circ g^{-1} \in S$, which agrees with the definition of an invariant subgroup.

$\Leftarrow$: Conversely, let's assume that S is an invariant subgroup but does not consist of complete classes of G . That means it is possible to find an element $g \in G$ and

Mathematica

GTLeftCosets, GTRightCosets

Install the point groups C_{4v} , C_s and C_{2v} .

```
In[8]:= c4v = GTInstallGroup[C4v, GOverbose -> False]
cs = {Ee, IC2a};
c2v = {Ee, C2z, IC2x, IC2y};
```

```
Out[8]:= {Ee, C2z, C4z^-1, C4z, IC2x, IC2a, IC2b, IC2y}
```

Calculate the left and right cosets for C_s .

```
In[11]:= GTLeftCosets[c4v, cs]
GTRightCosets[c4v, cs]
```

```
Out[11]:= {{C2z, IC2b}, {IC2x, C4z}, {IC2a, Ee}, {C4z^-1, IC2y}}
```

```
Out[12]:= {{C2z, IC2b}, {IC2x, C4z^-1}, {IC2a, Ee}, {C4z, IC2y}}
```

Calculate the left and right cosets for C_{2v} .

```
In[13]:= GTLeftCosets[c4v, c2v]
GTRightCosets[c4v, c2v]
```

```
Out[13]:= {{C2z, IC2x, IC2y, Ee}, {IC2a, C4z^-1, C4z, IC2b}}
```

```
Out[14]:= {{C2z, IC2x, IC2y, Ee}, {IC2a, C4z^-1, C4z, IC2b}}
```

Figure 3.7 Calculating the left and right cosets of the subgroups C_s and C_{2v} with respect to C_{4v} by applying **GTLeftCosets** and **GTRightCosets**.

$s \in S$ with the property $g \circ s \circ g^{-1} \notin S$, which is in contradiction to the assumption that S is an invariant subgroup. $\square$

A group is said to be simple, if it does not contain a proper invariant subgroup. If the group does not possess a proper Abelian invariant subgroup it is called semi-simple. A composite group has a proper invariant Abelian subgroup.

The center of a group is an invariant subgroup. The group $\mathcal{G}'$ is a normal divisor of its normalizer with respect to a corresponding supergroup $\mathcal{G}$: $\mathcal{G}' \triangleleft \mathcal{N}(\mathcal{G}'|\mathcal{G})$.

Example 9 (Coset decomposition of C_{4v}). The decomposition of a group $\mathcal{G}$ into left and right cosets can be calculated using **GTLeftCosets** and **GTRightCosets**. In Figure 3.7, an example for the group C_{4v} of the two subgroups $C_s = \{Ee, IC_{2a}\}$ and $C_{2v} = \{Ee, C_{2z}, IC_{2x}, IC_{2y}\}$ is shown. For the group C_s with group order $\text{ord}(C_s) = 2$ four left and four right cosets can be found. As can be verified, the left and right cosets differ from each other. In the case of C_{2v} with $\text{ord}(C_{2v}) = 4$ the two left and two right cosets are the same. Hence, C_{2v} is an invariant subgroup of C_{4v} .

Example 10 (Invariant subgroups of C_{4v}). Using **GTInvSubGroupQ**, it can be checked if $S \subset \mathcal{G}$ is an invariant subgroup of $\mathcal{G}$. To obtain all invariant subgroups of a group $\mathcal{G}$, **GTInvSubGroups** can be used. An example for the group C_{4v} is shown in Figure 3.8. In total, four invariant subgroups are found.

Mathematica

GTInvSubGroups, GTInvSubGroupQ

Install the group C_{4v} and calculate the classes.

```
In[8]:= c4v = GTInstallGroup[C4v];
GTClasses[c4v]
```

The standard representation has changed to $O(3)$

```
Out[9]:= {{Ee}, {IC2x, IC2y}, {IC2a, IC2b}, {C4z, C4z}, {C2z}}
```

Obtain all invariant subgroups by using **GTInvSubGroups**.

```
In[10]:= isg = GTInvSubGroups[c4v]; isg // MatrixForm
```

Out[10]//MatrixForm=

$$\begin{pmatrix} \{C_{2z}, Ee\} \\ \{C_{2z}, Ee, IC_{2x}, IC_{2y}\} \\ \{C_{2z}, Ee, IC_{2a}, IC_{2b}\} \\ \{C_{2z}, Ee, C_{4z}^{-1}, C_{4z}\} \end{pmatrix}$$

As can be seen, the invariant subgroups consist of complete classes of a group. To check if a subgroup is an invariant subgroup, **GTInvSubGroupQ** can be used

```
In[11]:= Map[GTInvSubGroupQ[c4v, #] &, isg]
```

```
Out[11]:= {True, True, True, True}
```

Figure 3.8 Determining the invariant subgroups of C_{4v} using **GTInvSubGroups**.

Task 9 (Properties of normal divisors). From the definition of normal divisors the following statements follow:

- All subgroups $\mathcal{U} \subseteq \mathcal{G}$ with index 2 are normal divisors.
- All Abelian subgroups of $\mathcal{G}$ are normal divisors.

Proof the two statements.

3.3

Quotient Groups

Quotient groups	
GTQuotientGroupQ	Checks if $S \subset \mathcal{G}$ can form a quotient group $\mathcal{G}/S$
GTQuotientGroup	Calculates the multiplication table of the quotient group $\mathcal{G}/S$

In terms of left cosets a group $\mathcal{G}$ can be decomposed with respect to a subgroup $S \subset \mathcal{G}$, as follows,

$$\mathcal{G} = g_1 S + g_2 S + \dots + g_N S, \quad N = \text{ind}(S). \quad (3.17)$$

The elements $g_i \in \mathcal{G}$ are the coset representatives. The set $\mathcal{G}/S = \{g_1 S, g_2 S, \dots, g_N S\}$ is called the *quotient set*. Considering the quotient set with respect to an invariant subgroup $\mathcal{N}$, it is possible to induce a group structure. Since $\mathcal{N}$ is an invariant subgroup, left and right cosets with respect to $\mathcal{N}$ are similar and the following equation holds,

$$a_i \mathcal{N} \circ a_j \mathcal{N} = (a_i \circ a_j) \mathcal{N}. \quad (3.18)$$

The above relation defines a group multiplication between cosets in terms of the coset representatives. In this case, $\mathcal{G}/\mathcal{N}$ forms a group, called the *quotient group*.²⁾ The identity element of the quotient group is the normal divisor $\mathcal{N}$. The order of the quotient group is $g/g_{\mathcal{N}} = \text{ord}(\mathcal{N})$.

Example 11 (The quotient group C_{4v}/C_4). The group $C_4 = \{Ee, C_{4z}, C_{4z}^{-1}, C_{2z}\}$ is an invariant subgroup of the group C_{4v} . Since $\text{ord}(C_4) = 4$, there are two cosets containing four elements each. In terms of the coset decomposition into left cosets, the group C_{4v} can be written as

$$C_{4v} = Ee C_4 + IC_{2a} C_4. \quad (3.19)$$

A GTPack example is shown in Figure 3.9. The quotient group is constructed using **GTQuotientGroup**. The group C_{4v}/C_4 is isomorphic to the group C_2 .

2) Quotient groups are also often called *factor groups*.

Mathematica**GTQuotientGroupQ, GTQuotientGroup**

Installation of the groups C_{4v} and C_4 .

```
In[8]:= c4v = GTInstallGroup[C4v, GVerbose -> False];
c4 = GTInstallGroup[C4, GVerbose -> False];
```

Check if the quotient group C_{4v}/C_4 can be formed.

```
In[10]:= GTQuotientGroupQ[c4v, c4]
```

```
Out[10]= True
```

Calculate the multiplication table of C_{4v}/C_4 .

```
In[11]:= GTQuotientGroup[c4v, c4];
```

Invariant subgroup $\mathcal{N} = \{Ee, C_{2z}, C_{4z}^{\frac{1}{2}}, C_{4z}\}$

Left cosets = $\left\{ \{C_{2z}, C_{4z}^{\frac{1}{2}}, C_{4z}, Ee\}, \{IC_{2x}, IC_{2a}, IC_{2b}, IC_{2y}\} \right\}$

	$C_{2z} \cdot \mathcal{N}$	$IC_{2x} \cdot \mathcal{N}$
$C_{2z} \cdot \mathcal{N}$	$C_{2z} \cdot \mathcal{N}$	$IC_{2x} \cdot \mathcal{N}$
$IC_{2x} \cdot \mathcal{N}$	$IC_{2x} \cdot \mathcal{N}$	$C_{2z} \cdot \mathcal{N}$

Figure 3.9 Calculate the multiplication table of the quotient group C_{4v}/C_4 using **GTQuotientGroup**.

By means of a homomorphism $f : \mathcal{G} \rightarrow \mathcal{H}$ it is possible to map a group $\mathcal{G}$ to a smaller group $\mathcal{H}$. The kernel (i.e., the set of all elements $g \in \mathcal{G}$ mapped to the identity element of $\mathcal{H}$) of the homomorphism is an invariant subgroup of the original group. The relation between $\mathcal{H}$ and $\mathcal{G}/\mathcal{K}$ is determined by the homomorphism theorem.

Theorem 10 (Homomorphism theorem). *Let $f : \mathcal{G} \rightarrow \mathcal{H}$ be a homomorphism with kernel $\mathcal{K}$ ($\mathcal{K} \triangleleft \mathcal{G}$). Then, the homomorphism $\overline{f} : \mathcal{G}/\mathcal{K} \rightarrow \mathcal{H}$, defined by $\overline{f}(g_i\mathcal{K}) = f(g_i)$, is an isomorphism and $\mathcal{G}/\mathcal{K} \cong \mathcal{H}$.*

Example 12 (Homomorphism theorem). Choosing $\mathcal{G} = D_{3h}$ and $\mathcal{H} = C_s$, a homomorphism can be defined by mapping all proper rotations within D_{3h} to Ee and all improper rotations to IC_{2y} . Hence, D_3 (the group containing all the proper rotations of D_{3h}) is a normal divisor of D_{3h} ($D_3 \triangleleft D_{3h}$) and represents the kernel of the mapping. The respective left and right cosets in $\mathcal{G}/\mathcal{K}$ are

$$(E, C_{2x}, C_{2A}, C_{2B}, C_{3z}, C_{3z}^{-1}), (IC_{2y}, IC_{2z}, IC_{2C}, IC_{2D}, IC_{6z}, IC_{6z}^{-1}). \quad (3.20)$$

This quotient group is isomorphic to C_s , i.e., $D_{3h}/D_3 \cong C_s$.

3.4

Product Groups

Product groups	
GTProductGroupQ	Checks if $\mathcal{G} = \mathcal{G}_1 \times \mathcal{G}_2$ or $\mathcal{G} = \mathcal{G}_1 \rtimes \mathcal{G}_2$
GTProductGroup	Forms the product of the groups $\mathcal{G}_1$ and $\mathcal{G}_2$

In the previous section, the notion of a quotient group was introduced. Subsequently, the concept of product groups is discussed, where two groups are combined to form a larger group.

Definition 17 (Direct product group). *Consider the groups $\mathcal{G}_1$ and $\mathcal{G}_2$ together with the corresponding multiplications $\circ$ and $\bullet$. The set of pairs $(g_1, g_2) \in \mathcal{G}_1 \times \mathcal{G}_2$ with $g_1 \in \mathcal{G}_1$ and $g_2 \in \mathcal{G}_2$ together with the multiplication relation $\cdot : \mathcal{G}_1 \times \mathcal{G}_2 \rightarrow \mathcal{G}_1 \times \mathcal{G}_2$ defined by*

$$(g_1, g_2) \cdot (g'_1, g'_2) = (g_1 \circ g'_1, g_2 \bullet g'_2) \quad g_1, g'_1 \in \mathcal{G}_1, \quad g_2, g'_2 \in \mathcal{G}_2, \quad (3.21)$$

is called the direct product group.

From the structure of direct product groups it follows that the group order is given by

$$\text{ord}(\mathcal{G}_1 \times \mathcal{G}_2) = \text{ord}(\mathcal{G}_1) \text{ord}(\mathcal{G}_2). \quad (3.22)$$

Furthermore, $\mathcal{G}_1 \times \mathcal{G}_2$ contains the subgroups $S_1 = \{(g_1, E_2) | g_1 \in \mathcal{G}_1\}$ and $S_2 = \{(E_1, g_2) | g_2 \in \mathcal{G}_2\}$, which are isomorphic to the groups $\mathcal{G}_1$ and $\mathcal{G}_2$, respectively. The elements of the two subgroups S_1 and S_2 commute and have only the identity element in common, $S_1 \cap S_2 = (E_1, E_2)$. Consequently, every element of $\mathcal{G}$ is a product of an element of S_1 and S_2

$$(g_1, g_2) = (g_1, E_2)(E_1, g_2). \quad (3.23)$$

The direct product group of two finite groups is again finite. Vice versa, in some cases finite groups can be expressed in terms of the direct product of two subgroups. For example, the crystallographic point group O_h , which is isomorphic to the direct product of T_d and C_s .

Theorem 11 (Direct product). *A group $\mathcal{G}$ is isomorphic to the direct product $\mathcal{G}_1 \times \mathcal{G}_2$ if the following conditions are satisfied:*

- $\mathcal{G}_1$ and $\mathcal{G}_2$ are two proper subgroups of $\mathcal{G}$,
- for all $g_1 \in \mathcal{G}_1$ and $g_2 \in \mathcal{G}_2$ the relation $g_1 \circ g_2 = g_2 \circ g_1$ holds,
- $\mathcal{G}_1 \cap \mathcal{G}_2 = \{E\}$,
- every element of $\mathcal{G}$ can be written as an element of $\mathcal{G}_1$ with an element of $\mathcal{G}_2$.

If the group $\mathcal{G}$ is isomorphic to $\mathcal{G}_1 \times \mathcal{G}_2$, we simply write $\mathcal{G} = \mathcal{G}_1 \times \mathcal{G}_2$ in the following. Furthermore, if $\mathcal{G}_1$ is an invariant subgroup ($\mathcal{G}_1 \triangleleft \mathcal{G}$) the product is called a *semidirect* product group and the notation $\mathcal{G} = \mathcal{G}_1 \rtimes \mathcal{G}_2$ is used. Among others, the structure of semidirect product groups occurs for symmorphic space groups, where the space groups can be written as the semidirect product of the group of pure translations and a point group. Space groups will be introduced in more detail in Section 4.2. The semidirect product structure allows for the application of the so-called method of induction for the calculation of matrices for irreducible representations as will be discussed in Section 5.7. The representation theory for symmorphic space groups as a consequence will be introduced in Section 6.4.

Example 13 (Product groups in GTPack). In Example 11 it was shown that the quotient group D_{3h}/D_3 is isomorphic to the group C_s . Analogously, it is possible to construct the group D_{3h} as a direct product of D_3 and C_s . An example by means of **GTPProductGroup** is shown in Figure 3.10. Since D_3 is an invariant subgroup of D_{3h} , it is possible to express D_{3h} as the semidirect product $D_{3h} = D_3 \rtimes C_s$.

Mathematica

GTPProductGroup, GTPProductGroupQ

Installation of the point groups D_3 and C_s .

```
In[8]:= d3 = GTInstallGroup[D3, GVerbose -> False]
       cs = GTInstallGroup[Cs, GVerbose -> False]
```

```
Out[8]:= {Ee, C2B, C2A, C2X, C3z^-1, C3z}
```

```
Out[9]:= {Ee, IC2z}
```

D_{3h} is given as a semi-direct product of D_3 and C_s .

```
In[10]:= prod = GTPProductGroup[d3, cs]
         semi-direct product
```

```
Out[10]:= {C2B, IC2D, IC6z, C3z^-1, IC6z^-1, C3z, C2A, IC2C, C2X, IC2Y, IC2z, Ee}
```

Check if the obtained group is given by D_{3h} .

```
In[11]:= d3h = GTInstallGroup[D3h, GVerbose -> False]
```

```
Out[11]:= {Ee, C2B, C2A, C2X, C3z^-1, C3z, IC2D, IC2C, IC2Y, IC2z, IC6z, IC6z^-1}
```

```
In[12]:= GTPProductGroupQ[d3h, d3, cs, GVerbose -> True]
         product group
```

```
Out[12]:= True
```

Figure 3.10 Application of **GTPProductGroup** to represent D_{3h} as the semidirect product $D_{3h} = D_3 \rtimes C_s$.

4

Discrete Symmetry Groups in Solid-State Physics and Photonics

Die Kristallographie, als Wissenschaft betrachtet, gibt zu ganz eigenen Ansichten Anlaß. Sie ist nicht produktiv, sie ist nur sie selbst und hat keine Folgen, besonders nunmehr, da man so manche isomorphe Körper angetroffen hat, die sich ihrem Gehalte nach ganz verschieden erweisen. Da sie eigentlich nirgends anwendbar ist, so hat sie sich in dem hohen Grade in sich selbst ausgebildet.

J.W. von Goethe

(Wilhelm Meisters Wanderjahre, 3. Buch, Aus Makaries Archiv 105)

Condensed matter systems exhibit a specific symmetry. Throughout this chapter an overview about several symmetry groups present in such systems is given. Point groups describe the local symmetry of an atom or impurity within a crystal or an atomic cluster. In three-dimensional crystals, for example, only 32 distinct point groups can be found. Some of them are isomorphic to each other. In 2 dimensions this number reduces to 10. Space groups describe the symmetry of lattice-periodic systems, i.e., crystals. Besides rotational symmetries these groups contain an infinite set of translational symmetries, mediated by the underlying lattice. Point and space groups can be extended by incorporating additional degrees of freedom, such as a magnetic moment. This leads to the concept of color or SHUBNIKOV groups. The chapter closes with a discussion of noncrystallographic groups present in carbon nanotubes and fullerenes.

With respect to the structure of crystalline materials and the corresponding group theoretical tools a large amount of software and databases are freely available. Prominent examples are given by:

- Bilbao crystallographic server [44]
- International Tables for Crystallography [45]
- Crystallography Open Database [46]
- Inorganic Crystal Structure Database (ICSD) FIZ Karlsruhe [47]
- The Cambridge Structural Database (CSD) [48].

The strength of GTPack lies in the connection between provided group theory commands and the programmable *Mathematica* environment. Interfaces between available databases and GTPack are developed. Structures can be imported and exported, e.g., to allow for the visualization of structures by means of tools like VESTA (Visualization for Electronic and STructural Analysis) [49]. The central part of this chapter is to provide the structural basics for Part Two and Three of this book.

4.1
Point Groups

Point groups	
GTShowSymmetryElements	Gives a graphical representation of symmetry elements
GTAllSymbols	Gives a list of all currently installed symmetry elements
GTInstallAxis	Installs a new axis together with the related symmetry elements
GTGroupConnection	Plots the subgroup relation within a list of groups
GTGroupHierarchy	Plots all sub- and supergroups of a group
GTGroupNotation	Switches notation between SCHÖNFLIES and HERMANN–MAUGUIN
GTPointGroups	Plots the subgroup relationships of the 32 crystallographic point groups

4.1.1
Notation of Symmetry Elements

Two notations are commonly used for the symmetry elements of point groups. The SCHÖNFLIES¹⁾ symmetry notation is frequently applied in connection to molecules and within solid-state physics. In contrast, the HERMANN–MAUGUIN²⁾ notation is used within the International Tables For X-ray Crystallography [40, 50].

The basics of both notations are summarized in Table 4.1.

The notation used in GTPack is based on the SCHÖNFLIES notation. In the cube shown in Figure 4.1a, twofold rotational axes connect the origin of the coordinate system with the edges of the cube (a, b, c, d, e, f). Additionally, threefold rotational axes passing through the origin and the corners of the cube ($\alpha, \beta, \gamma, \delta$), while the coordinate axes are passing through the faces of the cube are fourfold rotational axes. For the hexagon shown in Figure 4.1b, twofold rotational axes are given by the coordinate axes and the axes connecting the origin and the points A, B, C , and D .

1) ARTHUR MORITZ SCHÖNFLIES (1853–1928) was a Mathematician. He became known by his contributions to the field of crystallography.

2) CARL HERMANN (1898–1961) was a German physicist and crystallographer. CHARLES-VICTOR MAUGUIN (1878–1958) was a French mineralogist.

Table 4.1 SCHÖNFLIES (SFL) notation and HERMANN–MAUGUIN (HM) notation of point group elements. A correspondence of the labeling of rotations is also given in Table 4.2.

SFL	HM	Definition
E	1	Identity
C_n	n	Rotations through $2\pi/n$
C_n^{-1}	n_{n-1}	Rotations through $-2\pi/n$
σ	m	Reflection plane
σ_h	n/m	Horizontal reflection plane, the reflection plane is perpendicular to the axis of highest rotational symmetry
σ_v	nm	Vertical reflection plane, the reflection plane contains the axis of highest rotational symmetry
I	$\bar{1}$	Inversion: $x \rightarrow -x, y \rightarrow -y, z \rightarrow -z$
IC_n	$\bar{n}$	Rotoinversion, a rotation is followed by an inversion ($IC_{ni} = C_{ni}I$)

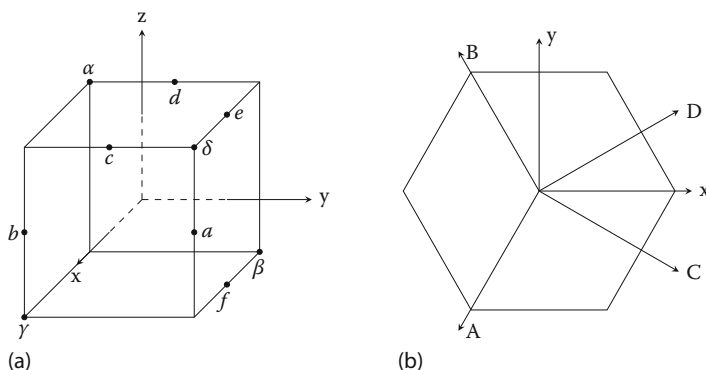


Figure 4.1 Illustration of high symmetry points and axes for a cube and for a hexagon. The labels are used for the denotation of symmetry elements in GTPack. (a) High symmetry points of a cube; (b) high symmetry points of a hexagon.

In GTPack reflection planes and improper rotations are expressed by a combination of proper rotations and inversion. Vice versa, the inversion itself can be expressed as a combination of a twofold rotation and a reflection. Consider for example a mirror operation σ_h with the mirror plane perpendicular to the z -axis. The resulting coordinate transformation is $x \rightarrow x, y \rightarrow y$, and $z \rightarrow -z$. A twofold rotation C_{2z} transforms $x \rightarrow -x, y \rightarrow -y$, and $z \rightarrow z$. Hence, a composition of both transformations leads to the inversion I transforming $x \rightarrow -x, y \rightarrow -y$, and $z \rightarrow -z$. Thus, the element σ_h can also be written as IC_{2z} . The concept can be extended to roto reflections, combinations of rotations and reflections. For fourfold and threefold roto reflections it follows,

$$\begin{aligned}
 S_{4z} &= \sigma_h C_{4z} = IC_{2z} C_{4z} = IC_{4z}^3 = IC_{4z}^{-1}, \\
 S_{3z} &= \sigma_h C_{3z} = IC_{2z} C_{3z} = IC_{6z}^3 C_{6z}^2 = IC_{6z}^5 = IC_{6z}^{-1}.
 \end{aligned}
 \tag{4.1}$$

Table 4.2 Comparison of proper and improper rotations in SCHÖNFLIES (SFL), HERMANN–MAUGUIN notation (HM), and the notation of GTPack (z-axis used as the reference).

Notation	Proper rotations						
SFL	C_2	C_3	C_3^{-1}	C_4	C_4^{-1}	C_6	C_6^{-1}
HM	2	3	3_2	4	4_3	6	6_5
GTPack	C2z	C3z	C3zi	C4z	C4zi	C6z	C6zi

Notation	Improper rotations						
SFL	σ	S_6^{-1}	S_6	S_4^{-1}	S_4	S_3^{-1}	S_3
HM	$\bar{2} \equiv m$	$\bar{3}$	$\bar{3}_2$	$\bar{4}$	$\bar{4}_3$	$\bar{6}$	$\bar{6}_5$
GTPack	IC2z	IC3z	IC3zi	IC4z	IC4zi	IC6z	IC6zi

On the basis of the relations, derived in (4.1), Table 4.2 compares the notation of proper and improper rotations in the different notation schemes.

The following basic operations occur in the 32 crystallographic point groups (powers of the elements are not listed). The notation is chosen with respect to Figure 4.1.

- $C_{3\alpha}, C_{3\beta}, C_{3\gamma}, C_{3\delta}$: $2\pi/3$ rotations. The elements are of order 3. The inverse elements are $C_{3\alpha}^{-1}, \dots$
- $C_{2x}, C_{2y}, C_{2z}, \dots C_{2f}$: π rotations. The elements are of order 2 and therefore inverse to itself.
- C_{4x}, C_{4y}, C_{4z} : $\pi/2$ rotations. The elements are of order 4. The inverse elements are $C_{4x}^{-1}, C_{4y}^{-1}, C_{4z}^{-1}$.
- C_{6z}, C_{3z} : $\pi/3$ and $2\pi/3$ rotations about the z-axis of the hexagon. The inverse elements are C_{6z}^{-1} and C_{3z}^{-1} , respectively.
- $C_{2A}, C_{2B}, C_{2C}, C_{2D}$: π rotations of a hexagon. The elements are inverse to themselves.

The improper rotations are defined by multiplication with I . All symmetry elements C_n and IC_n are automatically installed in GTPack for $n = 2, 3, \dots, 9$ and the axes according to Figure 4.1. Additional symmetry elements for additional axes can be installed using **GTInstallAxis**. All currently installed axes can be shown with **GTAllSymbols**. The elements can also be found on the palette of GTPack. Although, symmetry elements $C_n^m, n = 2, \dots, 9, m = 1, \dots, (n - 1)$ are installed in GTPack, only 2-, 3-, 4-, and 6-fold rotation axes can be members of crystallographic point groups due to the so-called crystallographic restriction. Consider as an example a regular pentagon, having a 5-fold rotation axis. It is not possible to cover the plane periodically by such regular pentagons. Rotational axes, not allowed in periodic solids, appear in molecules, graphene nanotubes, and buckyballs (cf. Section 4.4), or in quasicrystals. Quasicrystals show long-range order, but are not periodic.

Mathematica

GTInstallAxis

Symmetry elements for a new axis can be installed using GTInstallAxis.

```
In[8]:= GTInstallAxis["w", {1, 2, 3}]
```

The axis w was added to the variable axeslist!

```
In[9]:= GTGetMatrix[C3w] // MatrixForm
```

Out[9]/MatrixForm=

$$\begin{pmatrix} -\frac{11}{28} & \frac{3}{14} + \frac{3\sqrt{\frac{3}{14}}}{2} & \frac{9}{28} - \sqrt{\frac{3}{14}} \\ \frac{3}{14} - \frac{3\sqrt{\frac{3}{14}}}{2} & -\frac{1}{14} & \frac{9}{14} + \sqrt{\frac{3}{14}} \\ \frac{9}{28} + \sqrt{\frac{3}{14}} & \frac{9}{14} - \frac{\sqrt{\frac{3}{14}}}{2} & \frac{13}{28} \end{pmatrix}$$

```
In[10]:= C3w ◦ C6w
```

Out[10]= C_{2w}

Figure 4.2 Installation of new symmetry elements using GTInstallAxis.

In principle, two symmetry operations do not commute, but it is possible to formulate some helpful rules about the commutativity of symmetry elements.

1. The inversion commutes with all symmetry elements.
2. Rotations around the same axis commute, i.e., $C_{2z} \circ C_{6z} = C_{6z} \circ C_{2z}$.
3. Rotations around perpendicular axes commute, i.e., $C_{4x} \circ C_{2z} = C_{2z} \circ C_{4x}$.
4. Rotations around a certain axis commute with reflections corresponding to a plane perpendicular to the rotation axis, i.e., $C_{4z} \circ IC_{2z} = I \circ C_{4z} \circ C_{2z} = I \circ C_{2z} \circ C_{4z} = IC_{2z} \circ C_{4z}$.
5. Reflections with respect to perpendicular planes commute: $IC_{2x} \circ IC_{2z} = C_{2x} \circ C_{2z} = C_{2z} \circ C_{2x} = IC_{2z} \circ IC_{2x}$.

Example 14 (Installation of symmetry elements). Symmetry elements can be installed by means of **GTInstallAxis**. The command installs all elements C_n and IC_n , $n = 2, 3, \dots, 9$ for a specified axis. An example is shown in Figure 4.2. The name of the axis and the rotation axis itself have to be provided.³⁾

Task 10 (Product of mirror operations). Proof the following theorem:

The product of two different mirror operations σ_1 and σ_2 is a rotation. The axis of the rotation is the intersection line of the mirror planes. The rotation angle is twice the angle φ between the mirror planes. An interchange of the rotations in the product changes the sign of the rotation angle.

- 3) Some limitations have to be mentioned here. If a new axis is implemented, it is possible that not all combinations with already existing symmetry elements can be expressed in symbolic form. Calculations with the corresponding matrices are possible of course.

4.1.2

Classification of Point Groups

In the following, an overview of the classification of the 32 crystallographic point groups will be given. All point groups are implemented within GTPack and can be installed using **GTInstallGroup**. They can also be found on the group theory palette.

The 32 crystallographic point groups can be grouped into eight categories.

1. Point groups C_n :

These are cyclic groups of order n containing all elements belonging to an n -fold rotation axis. For a rotation axis a , the elements can be represented as C_{na}^m . It follows that the groups C_n are Abelian. The group $C_1 = \{E\}$ contains the identity only, i.e., the group denotes the absence of any symmetry.

$$\Rightarrow C_1, C_2, C_3, C_4, C_6 \quad 5 \text{ groups}$$

2. Point groups C_{nv} :

In addition to an n -fold rotation axis the group contains n vertical mirror planes. These mirror planes are generated from the n -fold rotational symmetry. An example for the point group C_{3v} is shown in Figure 4.3a. If n is even, the mirror planes are called $\sigma_v, \sigma_d, \sigma'_v, \sigma'_d, \dots$. In case of an odd n , the mirror planes are not distinguished explicitly, i.e., they are named $\sigma_v, \sigma'_v, \sigma''_v, \dots$. Every mirror plane can be transformed into another by means of a rotation. The order of the group is $2n$. C_{nv} is non-Abelian for $n > 2$.

$$\Rightarrow C_{2v}, C_{3v}, C_{4v}, C_{6v} \quad 4 \text{ groups}$$

3. Point groups C_{nh} :

The groups are generated by an n -fold rotation C_{na} and a mirror plane σ_h perpendicular to the rotation axis a . The order of the group is $2n$. Since C_{na} and σ_h commute, the groups C_{nh} are Abelian.

For odd n , the groups are cyclic. For even n they contain the inversion, since $C_{2k}^k \sigma_h = C_2 \sigma_h = I$. The group $C_{1h} = \{E, \sigma_h\} = \{E, IC_{2z}\}$ consists of the identity and a mirror plane. It is also called C_s .

$$\Rightarrow C_s, C_{2h}, C_{3h}, C_{4h}, C_{6h} \quad 5 \text{ groups}$$

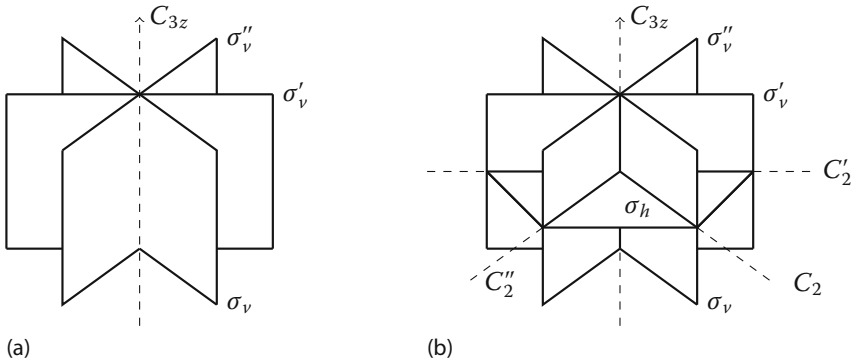


Figure 4.3 Illustration of symmetry elements within the point groups C_{3v} (a) and D_{3h} (b).

4. Point groups S_n :

The groups S_n are generated by a roto-reflection and are cyclic of order n . The group $S_2 = C_i = \{E, I\}$ only contains the identity and the inversion. The group S_6 is commonly known as C_{3i} .

$$\Rightarrow S_2, S_4, C_{3i} \quad 3 \text{ groups}$$

5. Dihedral groups D_n :

The dihedral groups are generated by an n -fold main rotation axis and a 2-fold rotation axis perpendicular to the main axis. The main rotation axis transforms the 2-fold axis in a set of n 2-fold axes. If n is even, two distinct sets of 2-fold rotations perpendicular to the main axis exist.

$$\Rightarrow D_2, D_3, D_4, D_6 \quad 4 \text{ groups}$$

6. Point groups D_{nd} :

The groups D_{nd} are generated by an n -fold main rotation axis, a 2-fold axis perpendicular to the main axis, and a mirror plane that contains the main axis and bisects the angle between two generated 2-fold axes. Because of the rotational symmetry n mirror planes $\sigma_d, \sigma'_d, \dots$ and n two-fold rotational axes are generated. The groups are non-Abelian groups of order $4n$.

$$\Rightarrow D_{2d}, D_{3d} \quad 2 \text{ groups}$$

7. Point groups D_{nh} :

The groups D_{nh} result from the groups D_n by adding a horizontal mirror plane σ_d . The groups are of order $4n$ and non-Abelian for $n > 2$.

$$\Rightarrow D_{2h}, D_{3h}, D_{4h}, D_{6h} \quad 4 \text{ groups}$$

8. Cubic point groups:

The last five point groups appear in the cubic crystal system. The groups are connected with symmetries of regular polyhedra. The properties of some polyhedra are given in Table 4.3. The group T_d contains the 24 symmetry elements leaving a tetrahedron invariant (cf. Figure 4.4). The group contains four 3-fold rotational axes through the corners and the middle of the respective opposite faces (eight symmetry operations). Six mirror planes contain two corners and bisect the respective opposite edges in the middle. Three axes, perpendicular to each other, bisect opposite edges. Three C_2 operations and six roto-reflections are connected with those axes. The subgroup of T_d containing only the proper rotations is of order 12 and called T . The group T_h is formed as a direct product of T and C_i . The group O_h contains all operations leaving the octahedron invariant and is of order 48. The subgroup of O_h containing only proper rotations is of order 24 and is named O .

$$\Rightarrow T_d, T_h, T, O_h, O \quad 5 \text{ groups}$$

All elements within the 32 point groups can be represented by 3-dimensional rotation matrices which are elements of the group $O(3)$. The group $SO(3)$ is a subgroup of $O(3)$ containing all proper rotations, represented by 3×3 matrices of determinant 1. $O(3)$ is the outer direct product of $SO(3)$ with $C_i = \{E, I\}$. The point groups are finite subgroups of $O(3)$ or $SO(3)$, respectively. The 11 proper point groups, containing only proper rotations, are the groups C_n , the dihedral groups D_n , as well as the groups T and O .

Table 4.3 Properties of regular polyhedra.

Polyhedron	Corners	Edges	Faces	Form of faces
Tetrahedron	4	6	4	Equilateral triangles
Cube	8	12	6	Squares
Octahedron	6	12	8	Equilateral triangles
Dodecahedron	20	30	12	Pentagons
Icosahedron	12	30	20	Equilateral triangles

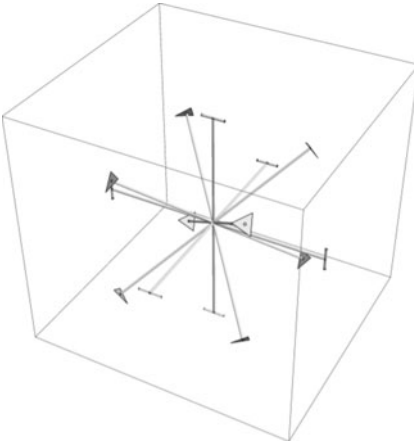


Figure 4.4 Twofold and threefold rotation axes of the point group T_d , illustrated using **GTShowSymmetryElements**.

All improper point groups can be constructed from the proper ones by one of the following two methods. First, the improper point group is the outer direct product of a proper point group with C_i , e.g., $O_h = O \times C_i$. Second, the proper point group is decomposed into cosets with respect to an invariant subgroup $\mathcal{N}$ of index 2, $\mathcal{G} = \mathcal{N} + a\mathcal{N}$. The improper point group is constructed as $\mathcal{G}' = \mathcal{N} + Ia\mathcal{N}$. For example, C_4 has C_2 as an invariant subgroup. The cosets with respect to the invariant subgroup are: $C_1 = (E, C_{2z})$, $C_2 = (C_{4z}, C_{4z}^{-1})$. Finally, the improper point group is $C_1 + IC_2 = \{E, C_{2z}, IC_{4z}, IC_{4z}^{-1}\}$, which gives the point group S_4 .

The 32 point groups can be constructed from a few generators, where the dimension of the basis is not larger than three. The generators of a group can be determined by means of **GTGenerators** as shown in Figure 3.3. Vice versa, a group can be installed from a set of generators using **GTGroupFromGenerators**.

Task 11 (Product of rotation and mirror operation). Proof the following theorem:

The product of a rotation C_n^m with a mirror operation σ_v results in a mirror operation. The mirror plane contains the rotation axis. For even n two sets of mirror planes exist ($\sigma_v, \sigma'_v, \dots$ and $\sigma_d, \sigma'_d, \dots$). The multiplication of the rotation with a member of one of the sets leads to another member of the same set. Demonstrate this result in the case of the benzene molecule.

Some of the point groups are related to each other by so-called subgroup chains $\mathcal{G} \supset \mathcal{G}' \supset \mathcal{G}'' \dots$. Figure 4.5 shows the hierarchy of all point groups. A similar representation can be obtained within GTPack by using **GTPointGroups** (see Figure 4.6). For a given set of point groups **GTGroupConnection** illustrates the relationship via subgroup chains of the given groups with each other (see Figure 4.7).

The command **GTGroupHierarchy** extracts from the graph of all subgroup chains all groups connected to a particular group, i.e., the illustrated groups are either subgroups or supergroups.

Besides the 32 point groups in three dimensions, there are ten point groups in two dimensions. A two-dimensional symmetry group has to be considered, e.g., in the case of surfaces of solids or a two-dimensional photonic crystal. A compact overview of the 2-dimensional point groups and their representation theory can be found in [51]. The subgroup chains of the 2-dimensional point groups are shown in Figure 4.6. Within the example, the SCHÖNFLIES and the HERMANN–MAUGUIN notation are used for comparison. To convert one notation into the other, **GTGroupNotation** can be applied.

The 32 crystallographic point groups are associated with seven crystal systems. For the representation of the symmetry elements in terms of matrices, it is possible to choose a natural basis such that all rotation matrices have only elements $-1, 0, 1$. The bases are described by a metric matrix (cf. [52]), where the trigonal and hexagonal system have the same matrix. Information about point groups and crystal systems are tabulated in Table 4.4. The command **GTCrystalSystem** can be applied to retrieve this information within GTPack. The section will be closed with the following definition.

Definition 18 (Holohedry). *The largest symmetry group of a crystal system is the holohedry group.*

4.2 Space Groups

4.2.1

Lattices, Translation Group

Definition 19 (Lattice). *A lattice is an infinite array of points in space. The lattice has the property of translational invariance, i.e., each lattice point has the same surrounding. A lattice can be constructed from a set of linear independent basis vectors. For a three-dimensional lattice all lattice points $\mathbf{t}_n$ can be obtained from three linear independent vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ as*

$$\mathbf{t}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, \quad n = (n_1, n_2, n_3), \quad n_i \in \mathbb{Z}. \quad (4.2)$$

Obviously, all translations $\mathbf{t}_n$ form a group which will be denoted by $\mathcal{T}$ in the following. $\mathcal{T}$ is a discrete and infinite group. In d dimensions, $\mathcal{T}$ is isomorphic to $\mathbb{Z}^d$. All translations $\mathbf{t}_n$ commute, i.e., $\mathcal{T}$ is Abelian. The introduction of periodic boundary conditions reduces the translation group to finite order as will be discussed in more detail in section 6.1.

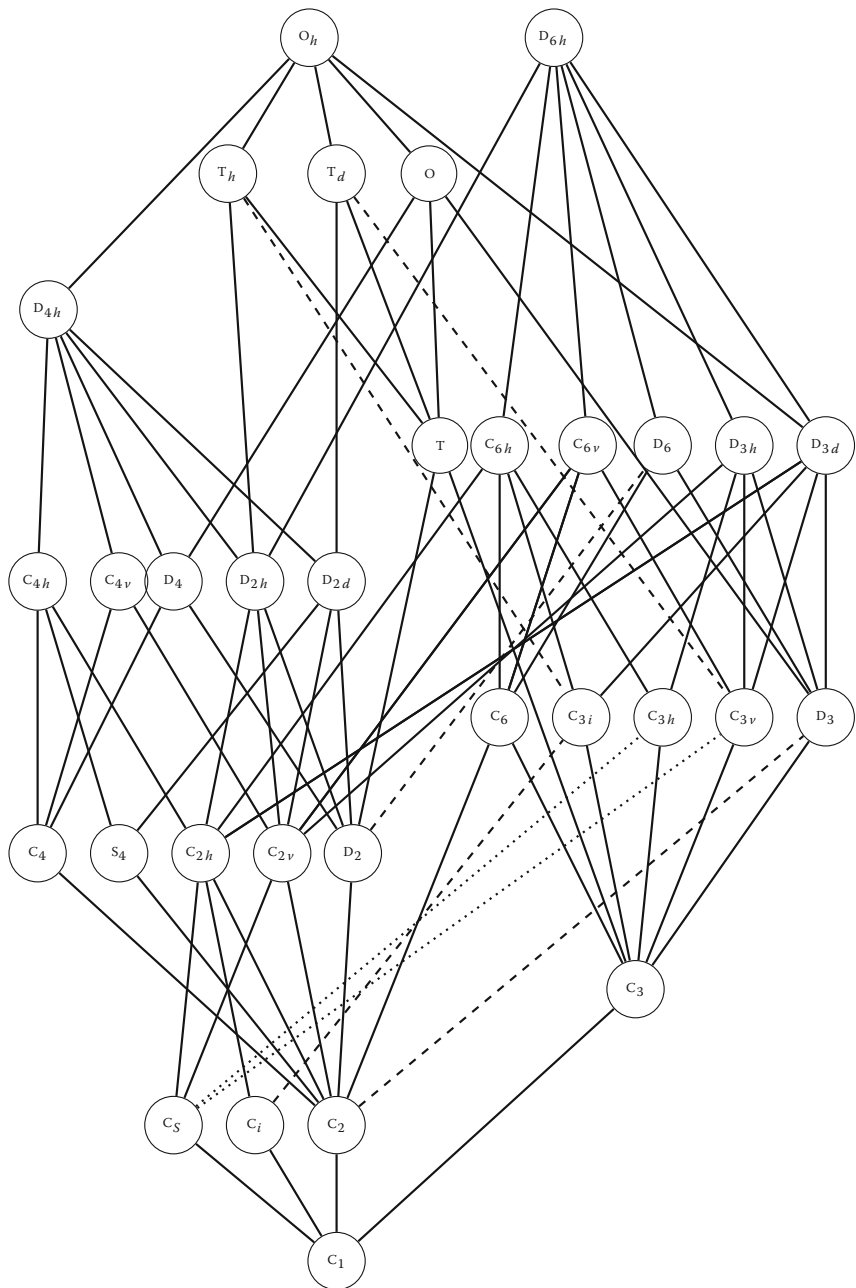


Figure 4.5 Subgroup hierarchy of the 32 point groups ($C_{3i} = S_6$). Dashed and dotted lines are used to increase the discriminability.

Mathematica**GTPointGroups**

```
In[8]:= GraphicsGrid[{{GTPointGroups["LayeredGraph", GODimension -> 2, GONotation -> "HM"],
GTPointGroups["LayeredGraph", GODimension -> 2, GONotation -> "SFL"]}}]
```

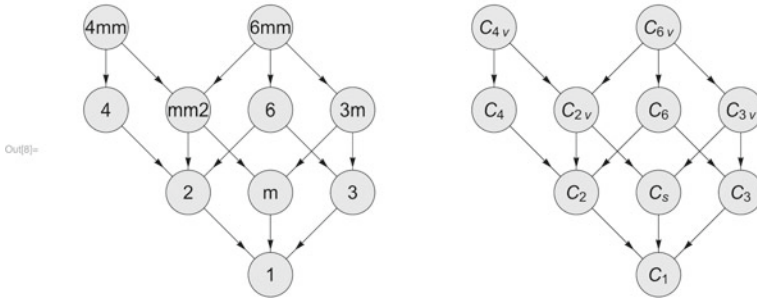


Figure 4.6 Relationships between the ten 2-dimensional point groups. The relationship between the ten groups is illustrated in HERMANN–MAUGUIN notation (left) and SCHÖNFLIES notation (right).

Mathematica**GTGroupConnection**

```
In[8]:= GTGroupConnection[{"D3h", "C3h", "C3", "C3v", "D3"}]
```

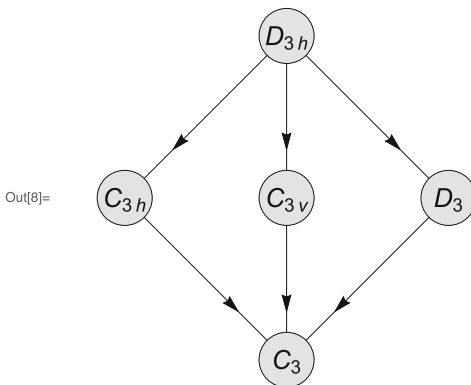


Figure 4.7 Relationships between the groups D_{3h} , C_{3h} , C_3 , C_{3v} and D_3 .

If a parallelepiped, constructed from the lattice vectors, generates the whole lattice by means of periodic repetition, the parallelepiped is named a unit cell. If the unit cell contains more than one lattice point it is called nonprimitive. Otherwise it is called primitive.

Table 4.4 The crystal systems.

Crystal system	Point groups	Metric matrix
Triclinic	C_1, C_i	$\begin{pmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{pmatrix}$
Monoclinic	C_2, C_s, C_{2h}	$\begin{pmatrix} g_{11} & g_{12} & 0 \\ g_{21} & g_{22} & 0 \\ 0 & 0 & g_{33} \end{pmatrix}$
Orthorhombic	D_2, C_{2v}, D_{2h}	$\begin{pmatrix} g_{11} & 0 & 0 \\ 0 & g_{22} & 0 \\ 0 & 0 & g_{33} \end{pmatrix}$
Tetragonal	$C_4, S_4, C_{4h}, D_4, C_{4v}, D_{2d}, D_{4h}$	$\begin{pmatrix} g_{11} & 0 & 0 \\ 0 & g_{11} & 0 \\ 0 & 0 & g_{33} \end{pmatrix}$
Trigonal Hexagonal	$C_3, C_{3i}, D_3, C_{3v}, D_{3d}$ $C_6, C_{3h}, C_{6h}, D_6, C_{6v}, D_{3h}, D_{6h}$	$\begin{pmatrix} g_{11} & -g_{11}/2 & 0 \\ -g_{11}/2 & g_{11} & 0 \\ 0 & 0 & g_{33} \end{pmatrix}$
Cubic	T, T_h, T_d, O, O_h	$\begin{pmatrix} g_{11} & 0 & 0 \\ 0 & g_{11} & 0 \\ 0 & 0 & g_{11} \end{pmatrix}$

4.2.2
Symmorphic and Nonsymmorphic Space Groups

Definition 20 (Space group). *The set of all coordinate transformations that map the equilibrium positions of an infinite crystalline solid into itself form a group called the space group.*

A space group containing an infinite number of transformations will be denoted by $\mathcal{R}$ in the following. Each element of $\mathcal{R}$ contains a rotational and a translational part (see Theorem 1). By denoting the primitive translations of the crystallographic lattice by $\mathbf{t}_n$, an element T of $\mathcal{R}$ can be written as $\{\underline{R}(T) \mid \mathbf{t}_T + \mathbf{r}_T\}$, where $\mathbf{r}_T$ denotes a nonprimitive translation.

Definition 21 (Symmorphic and nonsymmorphic space groups). *A space group $\mathcal{R}$ is called a symmorphic space group if $\mathbf{r}_T = \mathbf{0}$ for all $T \in \mathcal{R}$ and nonsymmorphic space group otherwise.*

In three dimensions there are in total 230 different space groups. A list of all space groups can be obtained by using the command `GTSpaceGroups` and setting the option `GOTable→True`. Only 73 of them are symmorphic space groups. An example for a 2-dimensional symmorphic space group (wallpaper group) is the square lat-

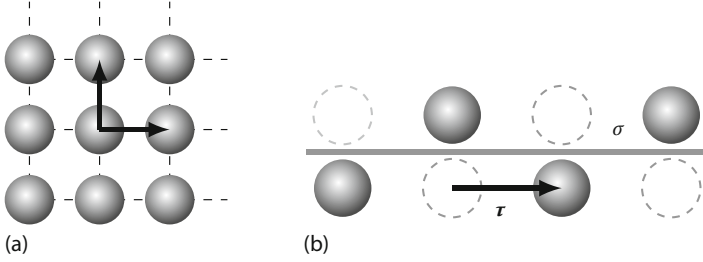


Figure 4.8 Examples for a symmorphic and a nonsymmorphic space group. (a) The one-atomic square lattice is an example for a symmorphic space group. (b) Nonsymmorphic

chain of atoms. A combination of reflection σ and nonprimitive translation τ leaves the chain invariant.

tice with one atom at each lattice site (see Figure 4.8a). If one of the lattice sites is considered as the center of the crystal, it can be verified that only rotations and reflections combined with primitive translations map the crystal into itself. An example for a nonsymmorphic crystal is the one-dimensional zigzag chain shown in Figure 4.8b. Whereas the reflection σ along a mirror axis in the center of the chain is not an element of the space group, a combination of σ together with a nonprimitive translation τ maps the crystal into itself and forms an element of the associated nonsymmorphic space group.

In connection to the space group $\mathcal{R}$ it is possible to introduce the group $\mathcal{G}_0$ of all rotational parts of the space group elements,

$$\mathcal{G}_0 = \{ \{ \underline{R}(T_1) \mid \mathbf{0} \}, \dots, \{ \underline{R}(T_N) \mid \mathbf{0} \} \mid T \in \mathcal{R} \}. \quad (4.3)$$

$\mathcal{G}_0$ is a subgroup of $\mathcal{R}$ for symmorphic space groups, but not for non-symmorphic space groups. In general it is not isomorphous to the holohedry group (Definition 18).

Theorem 12 ($\mathcal{T}$ is an invariant subgroup of $\mathcal{R}$). *The translation group $\mathcal{T}$ of all primitive lattice translations forms an invariant subgroup of the space group $\mathcal{R}$. The quotient group $\mathcal{R}/\mathcal{T}$ is isomorphic to $\mathcal{G}_0$.*

Proof. The first statement can be derived by calculating a conjugate element GTG^{-1} , $T \in \mathcal{T}$, $G \in \mathcal{R}$, and by showing that this element is an element of $\mathcal{T}$,

$$\{ \underline{R}(T) \mid \mathbf{t}_T + \mathbf{r}_T \} \{ \underline{1} \mid \mathbf{t}_n \} \{ \underline{R}(T) \mid \mathbf{t}_T + \mathbf{r}_T \}^{-1} = \{ \underline{1} \mid \underline{R}(T)\mathbf{t}_n \} \in \mathcal{T}. \quad (4.4)$$

To see that $\{ \underline{1} \mid \underline{R}(T)\mathbf{t}_n \}$ is indeed a lattice vector follows from the fact that GTG^{-1} has to be an element of $\mathcal{R}$ and that $\{ \underline{1} \mid \underline{R}(T)\mathbf{t}_n \}$ is a pure translation. Since $\mathcal{T}$ is an invariant subgroup of $\mathcal{R}$ it is possible to define the quotient group $\mathcal{R}/\mathcal{T}$ (see Section 3.3). Since $\mathcal{T}$ consists of pure translations, the left coset $\{ \underline{R}(T) \mid \mathbf{t}_T + \mathbf{r}_T \} \mathcal{T}$ is given by the set of all transformations with rotational part $\underline{R}(T)$. The same follows for a second element $\{ \underline{R}(T') \mid \mathbf{t}_{T'} + \mathbf{r}_{T'} \}$ forming the left

coset $\{\underline{R}(T') | \mathbf{t}_{T'} + \mathbf{r}_{T'}\} \mathcal{T}$. Suppose that $\underline{R}(T) \neq \underline{R}(T')$ then the product in the quotient group is given by

$$\begin{aligned} & (\{\underline{R}(T) | \mathbf{t}_T + \mathbf{r}_T\} \mathcal{T}) \circ (\{\underline{R}(T') | \mathbf{t}_{T'} + \mathbf{r}_{T'}\} \mathcal{T}) = \\ & \{\underline{R}(T)\underline{R}(T') | \underline{R}(T) \cdot (\mathbf{t}_T + \mathbf{r}_T) + \mathbf{t}_{T'} + \mathbf{r}_{T'}\} \mathcal{T}, \end{aligned} \quad (4.5)$$

giving the coset of all transformations with rotational part $\underline{R}(T)\underline{R}(T')$. $\square$

Determining a space group from an atomic cluster or reformulating a crystal structure by changing the unit cell is not addressed here. However, information of computer implementations can be found elsewhere [53–55]. For example, after finding the correct space group symmetry, the code *FINDSYM* [54] allows for an export of the crystal structure in terms of *cif*-files, which is a standard format to represent crystal structures. The import of such files using GTPack is discussed in the next section.

Example 15 (Space group notations and installation). Within the classification of the space groups by SCHÖNFLIES [56], the space groups are denoted with respect to their crystal class. As introduced in Section 4.1.2, there are 32 crystal classes which can be associated with 32 point groups. For example, there are ten nonequivalent space groups belonging to the cubic crystal class with point group O_h . They are denoted by $O_h^1, \dots, O_h^{10}$, where the groups O_h^1 , O_h^5 , and O_h^9 belong to the simple cubic, the face-centered cubic, and the body-centered cubic lattice having only atoms at the lattice points. The space group of the diamond structure having two atoms per lattice site is denoted by O_h^7 . An alternative to the SCHÖNFLIES notation is the *international notation*, which takes into account information about the generators of the space group [57]. This notation starts with a character denoting primitive (*P*), body centered (*I*), face centered (*F*), rhombohedral (*R*), or centered on *A*, *B*, or *C* faces (*A*, *B*, and *C*, respectively). Numbers denote the rotations ($360^\circ/n$) and numbers with a subscript denote screw axes (rotation + translation along the rotation axis). For example, 2_1 denotes a twofold rotation followed by a $1/2$ translation and 3_1 denotes a threefold rotation followed by a $1/3$ rd translation. The character *m* denotes a reflection plane. Glide planes (reflection + translation) are labeled by *a*, *b*, or *c* depending on the axis the glide is along. Furthermore, *n* denotes a glide translation along with half a face diagonal, *d* a glide plane with translation along a quarter of a face diagonal, and *e* two glides having the same glide plane and translation along two half-lattice vectors. Besides the international notation and the SCHÖNFLIES notation an indexing of the space groups with numbers $1, \dots, 230$ has been established. By applying the command **GTSpaceGroups**, the different notations for a particular space group can be obtained. Furthermore, it is stated whether the chosen space group is symmorphic or not. An example for the nonsymmorphic space group O_h^3 is shown in Figure 4.9. Analogously to point groups, space groups can be installed by applying the command **GTInstallGroup**. The output is the quotient group $\mathcal{R}/\mathcal{T}$.

Mathematica**GTSpaceGroups, GTInstallGroup**

Use GTSpaceGroup to get information about different notations of space groups.

```
In[10]:= GTSpaceGroups[|Pm - 3 n|, GOVBOSE -> True]
```

Number	System	Schoenflies	International	symmorphic
223	Cubic	O _h ³	Pm $\bar{3}$ n	no

```
Out[10]:= {223, Cubic, Oh3, Pm $\bar{3}$ n, no}
```

Space groups can be installed similarly to point groups by using GTInstallGroup.

```
In[11]:= GTInstallGroup[Oh3]
```

```
Out[11]:= { {Ee, {0, 0, 0}}, {C2z, {0, 0, 0}}, {C2y, {0, 0, 0}}, {C2x, {0, 0, 0}},
  {C3z-1, {0, 0, 0}}, {C3y-1, {0, 0, 0}}, {C3x-1, {0, 0, 0}}, {C3a-1, {0, 0, 0}},
  {C3b-1, {0, 0, 0}}, {C3y, {0, 0, 0}}, {C3a, {0, 0, 0}}, {C3b, {0, 0, 0}},
  {C2a, {1/2, 1/2, 1/2}}, {C2b, {1/2, 1/2, 1/2}}, {C4z, {1/2, 1/2, 1/2}}, {C4z-1, {1/2, 1/2, 1/2}},
  {C4x, {1/2, 1/2, 1/2}}, {C2e, {1/2, 1/2, 1/2}}, {C2f, {1/2, 1/2, 1/2}}, {C4x-1, {1/2, 1/2, 1/2}},
  {C4y-1, {1/2, 1/2, 1/2}}, {C2c, {1/2, 1/2, 1/2}}, {C4y, {1/2, 1/2, 1/2}}, {C2d, {1/2, 1/2, 1/2}},
  {IEe, {0, 0, 0}}, {IC2z, {0, 0, 0}}, {IC2y, {0, 0, 0}}, {IC2x, {0, 0, 0}},
  {IC3z-1, {0, 0, 0}}, {IC3y-1, {0, 0, 0}}, {IC3x-1, {0, 0, 0}}, {IC3a-1, {0, 0, 0}},
  {IC3b-1, {0, 0, 0}}, {IC3y, {0, 0, 0}}, {IC3a, {0, 0, 0}}, {IC3b, {0, 0, 0}},
  {IC2a, {1/2, 1/2, 1/2}}, {IC2b, {1/2, 1/2, 1/2}}, {IC4z, {1/2, 1/2, 1/2}}, {IC4z-1, {1/2, 1/2, 1/2}},
  {IC4x, {1/2, 1/2, 1/2}}, {IC2e, {1/2, 1/2, 1/2}}, {IC2f, {1/2, 1/2, 1/2}}, {IC4x-1, {1/2, 1/2, 1/2}},
  {IC4y-1, {1/2, 1/2, 1/2}}, {IC2c, {1/2, 1/2, 1/2}}, {IC4y, {1/2, 1/2, 1/2}}, {IC2d, {1/2, 1/2, 1/2}} }
```

Figure 4.9 Receiving information about the space group $Pm\bar{3}n$ by using GTSpaceGroups.⁴⁾

4.2.3

Site Symmetry, WYCKOFF Positions, and WIGNER-SEITZ Cell

A crystalline solid is a periodic arrangement of unit cells including a certain amount of atoms. The choice of the unit cell is not unique and in some cases it is even preferred to use large cells instead of small ones⁵⁾. A rather special choice is the so-called WIGNER-SEITZ cell, which contains only one lattice point and where each point within the interior of the cell is closer to this particular point than to any other lattice point of the crystal. Since a crystalline solid is anisotropic, not every point within the WIGNER-SEITZ cell or any cell in general has the same symmetry.

- 4) Bracketing bars are used for the space group symbols. They are given by Esc l| Esc and Esc r| Esc and can be found also on the group theory palette. Space group elements are written by means of AngleBrackets Esc < Esc and Esc > Esc.
- 5) For example, so-called super cells are used for the study of impurities [58, 59].

Definition 22 (Site symmetry group). *The site symmetry group $\mathcal{G}_{\mathbf{r}}$ of a point $\mathbf{r}$ within a crystalline solid is given by the set of all symmetry operations that leave the point invariant.*

Clearly, the site symmetry group $\mathcal{G}_{\mathbf{r}}$ is a subgroup of the space group $\mathcal{G}$. Two site symmetry groups $\mathcal{G}_{\mathbf{r}}$ and $\mathcal{G}_{\mathbf{r}'}$ are conjugate subgroups of $\mathcal{G}$ if

$$\mathcal{G}_{\mathbf{r}} = T \mathcal{G}_{\mathbf{r}'} T^{-1}, \quad T \in \mathcal{G}. \quad (4.6)$$

Definition 23 (WYCKOFF positions). *A WYCKOFF position is a point in the unit cell belonging to a set of points for which the site symmetry groups are conjugate subgroups of the space group $\mathcal{G}$.*

The number of conjugate subgroups to a certain position refers to the multiplicity of the WYCKOFF position. The higher the site symmetry the lower the multiplicity. The highest number of distinct WYCKOFF positions namely 27 can be found for the space group $Pmmm$. In total there are 1731 WYCKOFF positions within the 230 3-dimensional space groups. The WYCKOFF positions are denoted with small characters (a, b, ...) indexing the positions from highest to lowest symmetry.

Example 16 (WYCKOFF positions and crystallographic data). WYCKOFF positions are used for the classification of equivalent positions [60]. Especially for large unit cells, the crystallographic data is significantly simplified if instead of all contained atoms only all nonequivalent atoms are listed. By applying the symmetry operations of the crystal, the complete set can be reconstructed from this information. A standard format for handling crystallographic data is given by *cif*-files. Within these files the cell information, nonequivalent positions, and symmetry transformations are specified (among others). An example for the cubic phase of BaTiO_3 is illustrated in Figure 4.11. First, the content of the *cif*-file is printed. There are 48 symmetry elements listed that have to be applied on the three nonequivalent sites (Ba, Ti, O). As can be verified the multiplicity of the barium and the titanium site is 1, whereas the multiplicity of the oxygen site is 3. That

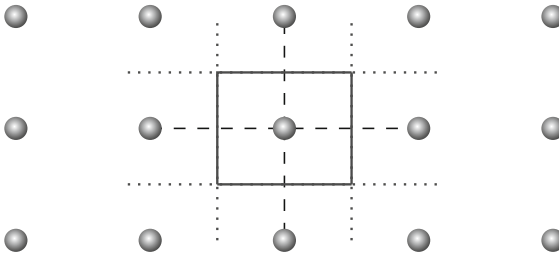


Figure 4.10 Construction of the WIGNER–SEITZ cell for a rectangular lattice. The procedure works as follows: Take one lattice site and connect it to all neighboring lattice sites. Within a 2-dimensional (3-dimensional) lattice, go

to the middle of each connecting line and construct an orthogonal line (plane). Take all crossing points of two lines (three planes) and form the convex hull.

Mathematica**GTImportCIF**

```

In[8]:= Import["BaTiO3.cif", "Table"] // TableForm
Out[8]//TableForm=

```

_chemical_formula_sum	BaTiO3				
_chemical_name_mineral	Barium	titanate			
_space_group_IT_number	221				
_symmetry_space_group_name_H-M	'P	m	-3	m'	
_cell_angle_alpha	90.				
_cell_angle_beta	90.				
_cell_angle_gamma	90.				
_cell_length_a	4.0073				
_cell_length_b	4.0073				
_cell_length_c	4.0073				
loop_					
_symmetry_equiv_pos_as_xyz					
x,y,z					
-y,x,z					
-x,-y,z					
y,-x,z					
x,-z,y					
x,-y,-z					
x,z,-y					
z,y,-x					
-x,y,-z					
-z,y,x					
z,x,y					
y,z,x					
-y,-z,x					
z,-x,-y					
-y,z,-x					
-z,-x,y					
-z,x,-y					
y,-z,-x					
y,x,-z					
-y,-x,-z					
-x,z,y					
-x,-z,-y					
z,-y,x					
-z,-y,-x					
-x,-y,-z					
y,-x,-z					
x,y,-z					
-y,x,-z					
-x,z,-y					
-x,y,z					
-x,-z,y					
-z,-y,x					
x,-y,z					
z,-y,-x					
-z,-x,-y					
-y,-z,-x					
y,z,-x					
-z,x,y					
y,-z,x					
z,x,-y					
z,-x,y					
-y,z,x					
-y,-x,z					
y,x,z					
x,-z,-y					
x,z,y					
-z,y,-x					
z,y,x					
loop_					
_atom_site_label					
_atom_site_fract_x					
_atom_site_fract_y					
_atom_site_fract_z					
_atom_site_symmetry_multiplicity					
_atom_site_Wyckoff_symbol					
Ba	0.5	0.5	0.5	1	b
Ti	0.	0.	0.	1	a
O	0.5	0.	0.	3	d

Import the cif-file and transform the information to GTPack standard form.

```

In[9]:= GTImportCIF["BaTiO3.cif"]
Out[9]= {{BaTiO3, Barium titanate}}, , , Pm3m, 221, {{a, 0, 0}, {0, a, 0}, {0, 0, a}},
  {{{{a, a, a}, Ba}, {(0, 0, 0), Ti}, {{a, 0, 0}, O}, {{0, a, 0}, O}, {{0, 0, a}, O}},
  {a -> 4.0073, cartesian}}
  10 000

```

Figure 4.11 Reading the information of a cif-file and transforming them to GTPack standard form using GTImportCIF.

means after applying the symmetry transformations, one barium, one titanium, and three oxygen atoms can be found in the unit cell. By using **GTImportCIF**, the import of such files is automatized and the transformations in the format used in GTPack are done automatically.

Example 17 (Construction of the WIGNER–SEITZ cell for a 2-dimensional lattice). The WIGNER–SEITZ cell for a specified lattice can be constructed in the framework of GTPack with the command **GTVoronoiCell**. The name VORONOI cell refers to a generalization of the WIGNER–SEITZ cell for a partition of a d -dimensional space into distinct regions around several points that do not necessarily need to be periodic. However, the implementation of the command is written for a periodic lattice. In Chapter 6.2, the reciprocal space will be introduced together with the reciprocal lattice of a crystal. The WIGNER–SEITZ cell of the reciprocal lattice is called the BRILLOUIN zone and can be constructed in the same way as explained here.

Mathematica

GTVoronoiCell

The lattice has to be specified by the basis.

```
In[8]:= lattice = {{1, 0}, {0.3, 1}};
```

Using GTVoronoiCell the Wigner-Seitz cell for the chosen lattice can be constructed.

```
In[9]:= GTVoronoiCell[lattice, {4, 2, 4}, {1}, GOBZPath → False]
```

Out[9]=

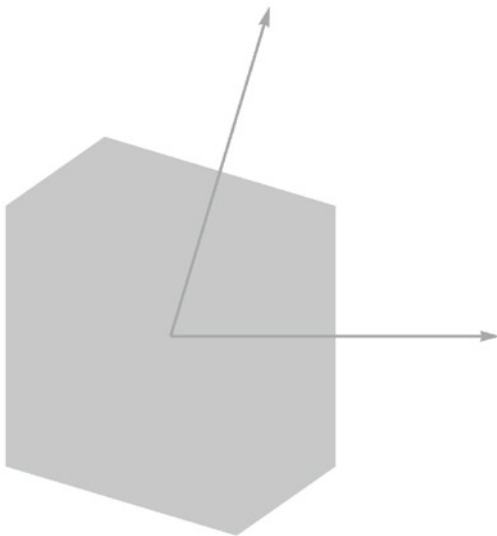


Figure 4.12 Construction of a 2-dimensional WIGNER–SEITZ cell using **GTVoronoiCell**.

For the example, a 2-dimensional lattice is considered, with a nonorthogonal basis, given by

$$\mathbf{a}_1 = (1, 0), \quad \mathbf{a}_2 = (0.3, 1). \quad (4.7)$$

The construction of the WIGNER–SEITZ cell follows the explanation within Figure 4.10. The application of **GTVoronoiCell** is shown in Figure 4.12. The first argument is the set of basis vectors of the lattice. The second is a list of three numbers $\{c, s_{\min}, s_{\max}\}$, with c as the cut-off radius for the cluster construction (number of considered lattice sites) as well as $s_{\min}$ and $s_{\max}$ as the minimal and maximal shell number for the lattice vectors to consider.⁶⁾ The third entry, which is not used within this example is for highlighting certain high-symmetry paths within the cell, as will be explained in Chapter 6.2.

4.3

Color Groups and Magnetic Groups

Color groups and magnetic groups	
GTMagetic	Switch to incorporate symmetry elements of magnetic groups

4.3.1

Magnetic Point Groups

In Section 1.2, it was demonstrated how an additional coloring scheme reduces the symmetry of a square. The color can be considered as an additional internal degree of freedom, e.g., the magnetic moment along the z -direction of an atom within magnetic structures. The color point groups are also named magnetic point groups or SHUBNIKOV groups⁷⁾.

In the following, these groups are introduced. In addition to spatial symmetry elements that form a point group, an operator $\hat{r}$ is introduced, changing the internal degree of freedom. For example, if a collinear magnetic structure is considered, $\hat{r}$ changes the direction of magnetic moments from up to down and vice versa. A color, for example, might change between black and white. The following three cases have to be distinguished.

1. SHUBNIKOV point groups of the first kind
SHUBNIKOV point groups of the first kind do not contain the operator $\hat{r}$. Therefore, the 32 ordinary point groups represent the SHUBNIKOV point groups of the first kind.

6) See also **GTLatCluster** and **GTLatShells** for details.

7) A. V. SHUBNIKOV (1887–1970), Russian crystallographer.

2. SHUBNIKOV point groups of the second kind (gray point group)

In SHUBNIKOV point groups of the second kind each point group element appears also connected with the operator $\hat{r}$.

$$\mathcal{M}_{\text{II}} = \mathcal{G} + \hat{r}\mathcal{G}, \quad \hat{r} \in \mathcal{M}_{\text{II}} \quad (4.8)$$

It follows that the ordinary point group $\mathcal{G}$ is an invariant subgroup of $\mathcal{M}_{\text{II}}$ of index 2. The coset decomposition in (4.8) defines the group $\mathcal{M}_{\text{II}}$. The order of $\mathcal{M}_{\text{II}}$ is $2g = 2 \text{ord}(\mathcal{G})$. Since $\hat{r}$ and the point group elements act in different spaces, they commute. Alternatively, $\mathcal{M}_{\text{II}}$ can be written as the direct product $\mathcal{M}_{\text{II}} = \mathcal{G} \times \{E, \hat{r}\}$. By construction $\mathcal{M}_{\text{II}}$ contains the two “colors” simultaneously. SHUBNIKOV groups of the second kind arise in connection to antiferromagnetic systems.

3. SHUBNIKOV point groups of the third kind

Let $\mathcal{N} \subset \mathcal{G}$ be an invariant subgroup of index 2 of the point group $\mathcal{G}$. A SHUBNIKOV group of third kind is constructed as

$$\mathcal{M}_{\text{III}} = \mathcal{N} + \hat{r}(\mathcal{G} - \mathcal{N}), \quad \hat{r} \notin \mathcal{G}, \quad \text{ord } \mathcal{M}_{\text{III}} = \text{ord } \mathcal{G}. \quad (4.9)$$

Since $\mathcal{N}$ is a subgroup of index 2, the number of group elements of $\mathcal{M}_{\text{III}}$ containing $\hat{r}$ is half the number of ordinary point group elements. All together 58 SHUBNIKOV point groups of the third kind exist.

Within GTPack SHUBNIKOV point groups can be installed by switching to magnetic groups using **GTMagentic**. This will be illustrated in Example 19.

Example 18 (Colored square). Referring to Section 1.2, the symmetry of a colored square is discussed in terms of SHUBNIKOV groups of the third kind. The symmetry group of the square is C_{4v} . The invariant subgroups of C_{4v} can be obtained using **GTInvSubGroups** as shown in Figure 4.13. It can be verified that C_{4v} has three invariant subgroups of index 2 (subgroups of order 4). The first one is $C_4 = \{Ee, C_{2z}, C_{4z}, C_{4z}^{-1}\}$. The other two are isomorphic and correspond to C_{2v} . Invariant subgroups of index 2 of C_4 and C_{2v} , are C_2 for C_4 and C_2 together with

Mathematica	
In[8]:=	<code>grp = GTInstallGroup[C4v]</code>
	The standard representation has changed to O(3)
Out[8]:=	$\{Ee, C_{2z}, C_{4z}, C_{4z}^{-1}, IC_{2x}, IC_{2a}, IC_{2b}, IC_{2y}\}$
	Calculate the invariant subgroups of C_{4v} .
In[9]:=	<code>GTInvSubGroups[grp]</code>
Out[9]=	$\left\{ \{C_{2z}, Ee\}, \{C_{2z}, Ee, IC_{2x}, IC_{2y}\}, \{C_{2z}, Ee, IC_{2a}, IC_{2b}\}, \{C_{2z}, Ee, C_{4z}^{-1}, C_{4z}\} \right\}$

Figure 4.13 Calculating the invariant subgroups of C_{4v} using **GTInvSubGroups**.

two isomorphic groups corresponding to C_s in the case of C_{2v} , respectively. The three invariant subgroups of C_{4v} lead to three different SHUBNIKOV groups of the third kind,

$$\begin{aligned}\mathcal{M}_{\text{III}}^1 &= \{E, C_{2z}, C_{4z}, C_{4z}^{-1}, \hat{r}IC_{2x}, \hat{r}IC_{2y}, \hat{r}IC_{2a}, \hat{r}IC_{2b}\}, \\ \mathcal{M}_{\text{III}}^2 &= \{E, C_{2z}, IC_{2x}, IC_{2y}, \hat{r}C_{4z}, \hat{r}C_{4z}^{-1}, \hat{r}IC_{2a}, \hat{r}IC_{2b}\}, \\ \mathcal{M}_{\text{III}}^3 &= \{E, C_{2z}, IC_{2a}, IC_{2b}, \hat{r}C_{4z}, \hat{r}C_{4z}^{-1}, \hat{r}IC_{2x}, \hat{r}IC_{2y}\}.\end{aligned}$$

Starting from the groups C_4 and C_{2v} the following SHUBNIKOV groups result,

$$\begin{aligned}\mathcal{M}_{\text{III}}^4 &= \{E, C_{2z}, \hat{r}C_{4z}, \hat{r}C_{4z}^{-1}\}, & \mathcal{M}_{\text{III}}^5 &= \{E, C_{2z}, \hat{r}IC_{2x}, \hat{r}IC_{2y}\}, \\ \mathcal{M}_{\text{III}}^6 &= \{E, C_{2z}, \hat{r}IC_{2a}, \hat{r}IC_{2b}\}, & \mathcal{M}_{\text{III}}^7 &= \{E, IC_{2x}, \hat{r}C_{2z}, \hat{r}IC_{2y}\}, \\ \mathcal{M}_{\text{III}}^8 &= \{E, IC_{2y}, \hat{r}C_{2z}, \hat{r}IC_{2x}\}, & \mathcal{M}_{\text{III}}^9 &= \{E, IC_{2a}, \hat{r}C_{2z}, \hat{r}IC_{2b}\}, \\ \mathcal{M}_{\text{III}}^{10} &= \{E, IC_{2b}, \hat{r}C_{2z}, \hat{r}IC_{2a}\}.\end{aligned}$$

Finally, the following magnetic point groups can be obtained starting from C_2 and C_{2v} ,

$$\begin{aligned}\mathcal{M}_{\text{III}}^{11} &= \{E, \hat{r}C_{2z}\}, & \mathcal{M}_{\text{III}}^{12} &= \{E, \hat{r}IC_{2x}\}, & \mathcal{M}_{\text{III}}^{13} &= \{E, \hat{r}IC_{2y}\}, \\ \mathcal{M}_{\text{III}}^{14} &= \{E, \hat{r}IC_{2a}\}, & \mathcal{M}_{\text{III}}^{15} &= \{E, \hat{r}IC_{2b}\}.\end{aligned}$$

The coloring schemes for some of the defined magnetic groups are shown in Figure 4.14. The corresponding subgroup chains can be derived from the above-defined groups,

$$\mathcal{M}_{\text{III}}^1 \supset \mathcal{M}_{\text{III}}^5 \supset \mathcal{M}_{\text{III}}^{12}, \quad \mathcal{M}_{\text{III}}^2 \supset \mathcal{M}_{\text{III}}^6 \supset \mathcal{M}_{\text{III}}^{14}, \quad \mathcal{M}_{\text{III}}^3 \supset \mathcal{M}_{\text{III}}^5 \supset \mathcal{M}_{\text{III}}^{13}. \quad (4.10)$$

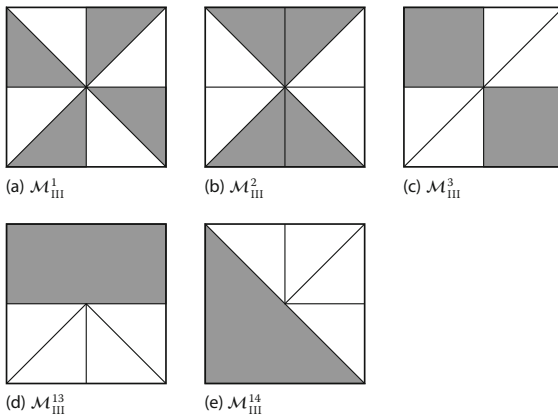


Figure 4.14 Coloring schemes corresponding to SHUBNIKOV groups of the third kind for a square.

Mathematica**GTMagnetic**

To allow for magnetic groups GTMagnetic has to be switched on.

```
In[8]:= GTMagnetic[True]
```

Rotation matrices now get an additional dimension for the intrinsic variable.

```
In[9]:= GTGetMatrix[C3z] // MatrixForm
```

```
Out[9]/MatrixForm=
```

$$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Elements including change of the internal variable are denoted with a prime.

```
In[10]:= GTGetMatrix[C3z'] // MatrixForm
```

```
Out[10]/MatrixForm=
```

$$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

Magnetic point groups can be installed, e.g., by using GTGroupFromGenerators.

```
In[11]:= GTGroupFromGenerators[{C4z', IC2a}]
```

```
Out[11]= {Ee, C2z, (IC2x)', (IC2y)', IC2a, IC2b, (C4z')', (C4z')}
```

Figure 4.15 Installation of magnetic point groups in GTPack.

Example 19 (Magnetic point groups in GTPack). As shown in Figure 4.15, **GTMagnetic** provides a switch to deal with magnetic groups. Symmetry elements including the change of the intrinsic variable are specified by a prime. Rotation matrices within GTPack get an additional dimension for this degree of freedom. Within the example, the group $\mathcal{M}_{\text{III}}^1$ is installed from the generators C_{4z} and $\hat{r}IC_{2a}$ (IC'_{2a}).

4.3.2

Magnetic Lattices

The pure translations of a lattice $\mathcal{T}$ form an Abelian group. Similarly to point groups, magnetic lattices can be constructed. An example for a black/white lattice is shown in Figure 4.16b. The construction starts from a primitive lattice as shown in Figure 4.16a, having three basis vectors **a**, **b**, and **c**. By introducing a second color in **a** direction, i.e., considering Figure 4.16b instead of Figure 4.16a, the unit cell is extended in **a**-direction and the new basis vectors are given by **a'** = 2**a**, **b**, and **c**. The full symmetry of the lattice in Figure 4.16b can be described by introducing

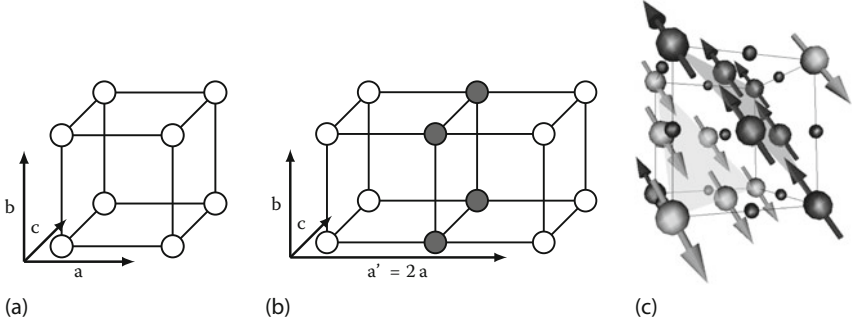


Figure 4.16 Construction of magnetic lattices [61]. (a) Primitive lattice; (b) colored lattice; (c) magnetic structure of NiO [62].

a combination of a translation $\mathbf{t}$ (which is equal to $\mathbf{a}$ in the example) with the color change operation $\hat{r}$. Hence, a colored lattice can be represented by the translation group

$$\mathcal{T}_{\text{IIb}} = \mathcal{T} + \hat{r} \{E|\mathbf{t}\} \mathcal{T}. \quad (4.11)$$

The notation $\mathcal{T}_{\text{IIb}}$ is explained in more detail during the next section where magnetic space groups are introduced. The magnetic BRAVAIS lattices for the 7 crystal systems are given in Table 4.5.

4.3.3

Magnetic Space Groups

Space groups describe the symmetry of lattice-periodic structures. Magnetic space groups or colored space groups describe the symmetry of periodic systems with an intrinsic variable, e.g., magnetic structures. The magnetic structure of NiO is shown in Figure 4.16c. The symmetry elements leaving the NiO structure invariant consist of translations, rotations, and reflections as well as combinations of those with a flip of the magnetic moment. The classification of magnetic space groups follows the classification of magnetic point groups described in Section 4.3.1. In the following, a space group is denoted by $\mathcal{R}$.

1. SHUBNIKOV space groups of the first kind

A SHUBNIKOV space group of the first kind does not contain the operator $\hat{r}$ and is given by $\mathcal{R}$ itself,

$$\mathcal{M}_I = \mathcal{R}. \quad (4.12)$$

2. SHUBNIKOV space groups of the second kind (gray space groups)

A SHUBNIKOV space group of the second kind contains all elements of $\mathcal{R}$ plus all elements of $\mathcal{R}$ combined with the operator $\hat{r}$.

$$\mathcal{M}_{II} = \mathcal{R} + \hat{r} \mathcal{R}, \quad \hat{r} \in \mathcal{M}_{II}. \quad (4.13)$$

Table 4.5 Magnetic BRAVAIS lattices. Columns 2 and 3 show the notation and basis vectors of the BRAVAIS lattice for a colored structure. Column 4 gives the notation of the magnetic lattice and column 5 the translation combined with the color inversion operator [61].

Crystal system	BRAVAIS lattice	Basis vectors	Magnetic lattice	Translation t
Triclinic	P_{2a}	$2\mathbf{a}, \mathbf{b}, \mathbf{c}$	P_a	$\mathbf{a}'/2$
Monoclinic	P_{2a}	$2\mathbf{a}, \mathbf{b}, \mathbf{c}$	P_a	$\mathbf{a}'/2$
	P_{2c}	$\mathbf{a}, \mathbf{b}, 2\mathbf{c}$	P_c	$\mathbf{c}'/2$
	P_A	$\mathbf{a}, \mathbf{b} + \mathbf{c}, \mathbf{b} - \mathbf{c}$	A_b	$\mathbf{b}'/2$
	A_{2a}	$2\mathbf{a}, \mathbf{b}, \mathbf{c}$	A_a	$\mathbf{a}'/2$
	A_P	$\mathbf{a}, \mathbf{b} + \mathbf{c}, \mathbf{b} - \mathbf{c}$	P_A	$(\mathbf{b}' + \mathbf{c}')/2$
Orthorhombic	P_{2a}	$2\mathbf{a}, \mathbf{b}, \mathbf{c}$	P_a	$\mathbf{a}'/2$
	P_C	$\mathbf{a} + \mathbf{b}, \mathbf{a} - \mathbf{b}, \mathbf{c}$	C_a	$\mathbf{a}'/2$
	P_F	$\mathbf{a} + \mathbf{b}, \mathbf{b} + \mathbf{c}, \mathbf{c} + \mathbf{a}$	F_s	$(\mathbf{a}' + \mathbf{b}' + \mathbf{c}')/2$
	C_{2c}	$\mathbf{a}, \mathbf{b}, 2\mathbf{c}$	C_c	$\mathbf{c}/2$
	CP	$\mathbf{a} + \mathbf{b}, \mathbf{a} - \mathbf{b}, \mathbf{c}$	P_C	$(\mathbf{a}' + \mathbf{b}')/2$
	C_I	$\mathbf{a} + \mathbf{b}, \mathbf{b} + \mathbf{c}, \mathbf{c} + \mathbf{a}$	I_C	$(\mathbf{a}' + \mathbf{b}')/2$
	F_C	$\mathbf{a}, \mathbf{b} + \mathbf{c}, \mathbf{b} - \mathbf{c}$	C_A	$(\mathbf{b}' + \mathbf{c}')/2$
	IP	$\mathbf{a} + \mathbf{b}, \mathbf{b} + \mathbf{c}, \mathbf{c} + \mathbf{a}$	P_I	$(\mathbf{a}' + \mathbf{b}' + \mathbf{c}')/2$
Tetragonal	P_{2c}	$\mathbf{a}, \mathbf{b}, 2\mathbf{c}$	P_c	$\mathbf{c}'/2$
	P_C	$\mathbf{a} + \mathbf{b}, \mathbf{a} - \mathbf{b}, \mathbf{c}$	P_C	$(\mathbf{a}' + \mathbf{b}')/2$
	P_I	$\mathbf{a} + \mathbf{b}, \mathbf{b} + \mathbf{c}, \mathbf{c} + \mathbf{a}$	I_c	$\mathbf{c}'/2$
	IP	$\mathbf{a} + \mathbf{b}, \mathbf{b} + \mathbf{c}, \mathbf{c} + \mathbf{a}$	P_I	$(\mathbf{a}' + \mathbf{b}' + \mathbf{c}')/2$
Trigonal	R_R	$\mathbf{a} + \mathbf{b}, \mathbf{b} + \mathbf{c}, \mathbf{c} + \mathbf{a}$	R_I	$(\mathbf{a}' + \mathbf{b}' + \mathbf{c}')/2$
Hexagonal	P_{2c}	$\mathbf{a}, \mathbf{b}, 2\mathbf{c}$	P_c	$\mathbf{c}'/2$
Cubic	P_F	$\mathbf{a} + \mathbf{b}, \mathbf{b} + \mathbf{c}, \mathbf{c} + \mathbf{a}$	F_S	$(\mathbf{a}' + \mathbf{b}' + \mathbf{c}')/2$
	IP	$\mathbf{a} + \mathbf{b}, \mathbf{b} + \mathbf{c}, \mathbf{c} + \mathbf{a}$	P_I	$(\mathbf{a}' + \mathbf{b}' + \mathbf{c}')/2$

3. SHUBNIKOV space groups of the third kind

SHUBNIKOV space groups of the third kind are divided into two classes. In the first class, the color inversion is connected to an element of the point groups, whereas in the second class, the color inversion is coupled with the lattice.

- a) $\mathcal{N}$ is an invariant subgroup of $\mathcal{R}$ of index 2 and does not contain pure translations. The SHUBNIKOV space group $\mathcal{M}_{\text{IIIa}}$ is constructed as

$$\mathcal{M}_{\text{IIIa}} = \mathcal{N} + \hat{r}(\mathcal{R} - \mathcal{N}), \quad \hat{r} \notin \mathcal{R}. \quad (4.14)$$

- b) The color inversion operator $\hat{r}$ is connected with the lattice as described in Section 4.3.2 and given by formula (4.11). Let $\mathcal{R}'$ be a space group that does

not contain the translation $\mathbf{t}$. Then, the SHUBNIKOV space group $\mathcal{M}_{\text{IIIb}}$ is constructed as

$$\mathcal{M}_{\text{IIIb}} = \mathcal{R}' + \hat{\tau} \{E|\mathbf{t}\} \mathcal{R}' . \quad (4.15)$$

Dia- and paramagnetic structures are described with SHUBNIKOV space groups of the second kind. Antiferromagnetic structures exhibit symmetries according to SHUBNIKOV groups of the kinds I, IIIa, and IIIb. Ferro- and ferrimagnetic structures are described by SHUBNIKOV groups of the kinds I and IIIa.

4.4

Noncrystallographic Groups, Buckyballs, and Nanotubes

Nanotubes, Buckyballs	
GTBuckyBall	Creates a C_{60} molecule
GTTubeParameters	Characteristic parameters of (n, m) nanotubes
GTTubeStructure	Structure of a nanotube
GTSymmetryElementQ	Checks if a symmetry element leaves a structure invariant
GTIcosahedronAxes	Installation of new axes for the groups I and I_h

Finally, the structure of carbon nanotubes and fullerenes will be discussed. Detailed information about properties of graphene, single-walled carbon nanotubes, and fullerenes can be found in [63–65]. To describe the symmetry of nanotubes and fullerenes, other groups than the 32 crystallographic point groups mentioned so far, have to be considered.

4.4.1

Structure and Group Theory of Nanotubes

A cylindrical graphene sheet with a diameter of about 0.7–10 μm is called a single-walled nanotube. Usually the ends of the cylinder are capped by hemispherical fullerene structures. Assuming a high aspect ratio (diameter/length) the influence of the caps can be neglected. Therefore, the nanotube can be considered as a one-dimensional nanostructure.

The construction of nanotubes starts with the honeycomb lattice. The basis vectors of the lattice are given by

$$\mathbf{a}_1 = \left(\frac{\sqrt{3}}{2}, \frac{1}{2} \right) a, \quad \mathbf{a}_2 = \left(\frac{\sqrt{3}}{2}, -\frac{1}{2} \right) a . \quad (4.16)$$

The two carbon atoms of the basis are located at

$$\mathbf{r}_1 = (0, 0)a, \quad \mathbf{r}_2 = \left(\frac{\sqrt{3}}{2}, 0 \right) a . \quad (4.17)$$

Mathematica	
GTubeParameters	
In[8]:= tube = GTubeParameters[9, 0, GVerbose → True];	
Property	Value
lattice constant	1
Chiral vector C_h (in units a_1, a_2)	{9, 0}
Length of C_h (units of a)	9
Diameter (units of a)	$\frac{9}{\pi}$
chiral angle θ	0
Translational vector T (in units a_1, a_2)	{1, -2}
Length of T (units of a)	$\sqrt{3}$
Number of hexagons N in unit cell	18
Symmetry vector R (in units a_1, a_2)	{1, -1}
Pitch τ of R	$\frac{\sqrt{3}}{2}$
Rotation angle ψ	$\frac{\pi}{9}$
Number M of T in $N \cdot R$	9

Figure 4.17 Structural parameters for an $(n, m) = (9, 0)$ zigzag nanotube.

A rectangular region is cut out of the lattice and rolled up to form the nanotube. Two vectors define the orientation and size of the rectangular region. The chiral vector

$$C_h = n \mathbf{a}_1 + m \mathbf{a}_2, \quad (n, m \in \mathbb{Z}, 0 \leq |m| \leq n) \quad (4.18)$$

defines the equator of the nanotube. The translational vector T , perpendicular to C_h ,

$$T = t_1 \mathbf{a}_1 + t_2 \mathbf{a}_2, \quad t_1 = \frac{2m + n}{g(m, n)}, \quad t_2 = -\frac{2n + m}{g(m, n)} \quad (4.19)$$

defines the axis of the nanotube.⁸⁾ The so-called chiral angle θ is defined by the angle of C_h with respect to $\mathbf{a}_1$:

$$\cos \theta = \frac{C_h \cdot \mathbf{a}_1}{|C_h| |\mathbf{a}_1|} = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}. \quad (4.20)$$

The structure of the nanotube is defined by the integers n, m , i.e., the symbol (n, m) is used to characterize the structure. **GTubeParameters** provides a list of characteristic quantities of a nanotube (cf. Figure 4.17). A more detailed discussion of those quantities can be found in [66].

Because of the construction principle, three types of nanotubes can be distinguished:

8) The function $g(m, n)$ is defined by the greatest common divisor (GCD) as: $g(m, n) = \text{GCD}[2m + n, 2n + m]$.

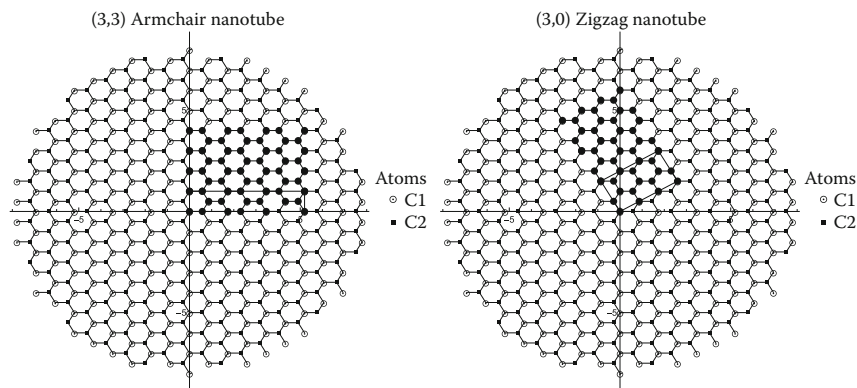


Figure 4.18 Construction of carbon nanotubes by cutting a rectangular region out of a graphene layer. The procedure is demonstrated for (3,3) armchair and (3,0) zigzag nanotubes. Three unit cells of the tubes are cut out.

1. armchair nanotubes, characterized by $n = m$ in (4.18),
2. zigzag nanotubes, defined by $n \neq 0, m = 0$,
3. chiral nanotubes, defined by $n \neq m \neq 0$.

Figure 4.18 demonstrates the construction of armchair and zigzag nanotubes. For zigzag nanotubes the chiral angle is $\theta = 0$, whereas it is $\theta = \pi/6$ for the armchair nanotubes.

The unit cell for a carbon nanotube can be constructed using **GTubeStructure** (cf. [67]). Final results for various examples can be seen in Figure 4.19. The naming convention due to the cross section of the nanotube can be verified from Figures 4.18 and 4.19.

Task 12 (Symmetry of (3,3)-nanotube). Construct a (3,3)-nanotube. Implement the group D_3 . Take a representative part of the nanotube and show that the nanotube is invariant under the symmetry elements of D_3 . Is the product group $D_3 \times C_i$ also a symmetry group of the nanotube? (Use **GTSymmetryElementQ**)

HINT: After construction, the nanotube has to be rotated slightly, such that the symmetry elements can be applied appropriately.

The symmetry groups of nanotubes depend on their particular structure. The achiral structures (armchair, zigzag) belong to symmorphic space groups while the space groups of the chiral nanotubes are nonsymmorphic. The discussion here is focused on the achiral structures. Figure 4.19 shows that achiral nanotubes are characterized by an n -fold principal rotation axis C_{nz} . Additionally, n twofold rotation axes perpendicular to the principal axis appear. The twofold axes intersect a C–C bond and the center of a hexagon on the opposite site of the tube. The rotational axes form a group D_n . Obviously, the group D_n has two generators C_{nz} and a twofold rotation, e.g., C_{2x} . The group is non-Abelian for $n > 2$ and its order is $2n$.

Mathematica
GTTubeStructure

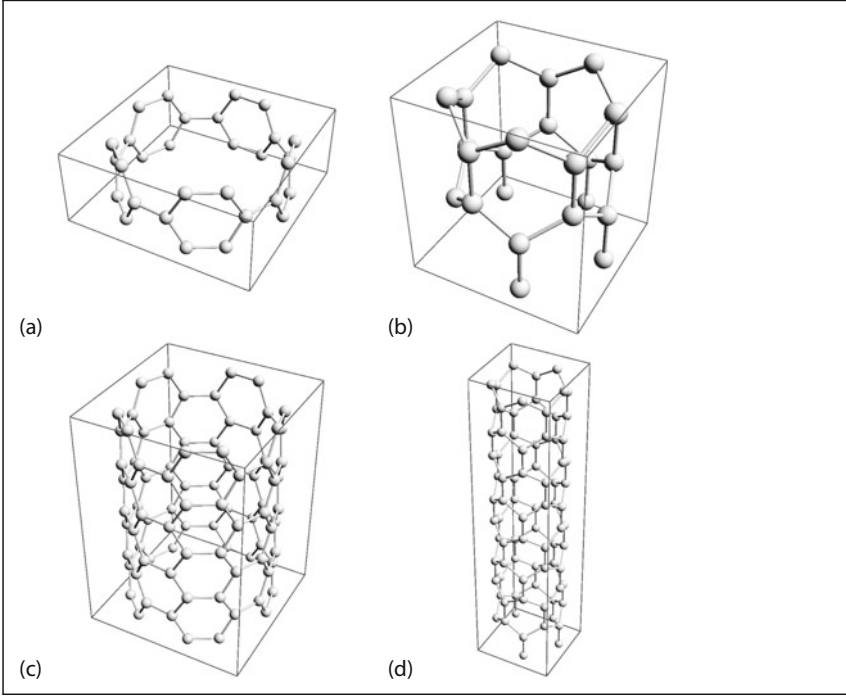


Figure 4.19 Structure of nanotubes. (a) One unit cell, (c) three unit cells of a (5,5) armchair nanotube; (b) one unit cell, (d) three unit cells of a (5,0) zigzag nanotube.

As soon as the generators are known, these groups can be installed within GT-Pack using **GTGroupFromGenerators** (cf. Figure 4.20). In some cases, additional axes need to be installed using **GTInstallAxis** to obtain symbols for all elements within the installed group (see Example 14).

The table in Figure 4.20 provides some properties of the groups D_n . The number of classes is $(n + 3)/2$ for odd n and $(n + 6)/2$ for even n . For odd n , the twofold rotation axes form a separate class. It is obvious that for odd n , $(n - 1)/2$ classes appear containing the rotations about the principal axis. Rotations C_{nz}^m and C_{nz}^{n-m} form a class. The class structure is different for even n . In this case, the twofold axes form two classes with $n/2$ elements. The rotation $C_{nz}^{n/2}$ forms its own class.

From Figure 4.19 it can be seen that the achiral nanotubes contain an inversion center. That means, the whole symmetry group is given by the direct product group of D_n with C_i

$$D_n \times C_i = \begin{cases} D_{nh} & \text{even } n \\ D_{nd} & \text{odd } n \end{cases} . \quad (4.21)$$

Mathematica

Install the groups D_n , $n=3..7$ from generators and find the orders of the group

```
In[8]:= mat1 = {GTGetMatrix[C3z], GTGetMatrix[C4z],
               GTGetMatrix[C5z], GTGetMatrix[C6z],
               GTGetMatrix[C7z]};
mat2 = GTGetMatrix[C2x]; groups = {};
Do[
  grp = Simplify[#] & /@ GTGroupFromGenerators[{mat1[[i]], mat2}];
  groups = Append[groups, grp]
  , {i, 1, 5}];
go = GTGroupOrder[#, GVerbose → False] & /@ groups;
gorder = {{ "D3", "D4", "D5", "D6", "D7"}, go} // Transpose
Out[10]:= {{D3, 6}, {D4, 8}, {D5, 10}, {D6, 12}, {D7, 14}}
```

Discussion of the class structure for the groups D_n

```
In[11]:= table = {};
classes = GTClasses[#] & /@ groups;
numcls = Length[#] & /@ classes;
Do[elem = Length[#] & /@ classes[[i]];
  ordelm = GTOrderOfElement[#[[1]]] & /@ classes[[i]];
  line = {gorder[[i, 1]], gorder[[i, 2]], numcls[[i]], elem, ordelm};
  table = Append[table, line], {i, 1, 5}];

In[13]:= head = {"group", "order", "classes", "elements /class", "order/class"};

In[14]:= Grid[Join[{head}, table],
  Frame → All, Alignment → Center,
  Dividers → {2 → GTDividerColor1, {2 → GTDividerColor1}},
  Background → {None, {1 → GTBackGroundColor1}}]
```

	group	order	classes	elements /class	order/class
	D ₃	6	3	{1, 2, 3}	{1, 3, 2}
	D ₄	8	5	{1, 2, 2, 2, 1}	{1, 2, 2, 4, 2}
	D ₅	10	4	{1, 2, 2, 5}	{1, 5, 5, 2}
	D ₆	12	6	{1, 2, 2, 3, 3, 1}	{1, 3, 6, 2, 2, 2}
	D ₇	14	5	{1, 2, 2, 2, 7}	{1, 7, 7, 7, 2}

Figure 4.20 Implementation and properties of the groups D_n .

4.4.2

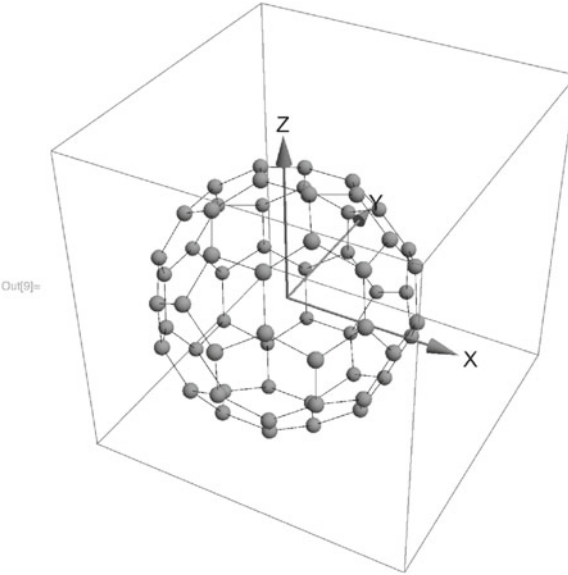
Buckminsterfullerene C_{60}

The symmetry group of the Buckminsterfullerene C_{60} (buckyball) is the icosahedral group I_h . In the following the installation of the groups I and I_h is shown. The buckyball itself is constructed by a method described by SENN [68] (cf. Figure 4.21).

Within the chosen orientation of the C_{60} molecule, the Cartesian axes are twofold symmetry axes. C_{60} has the structure of a truncated icosahedron. The cuts are performed perpendicular to the fivefold axes of the icosahedron. If the length of the icosahedron edges is a , the construction creates two edges of different length $r_5 = (1 + \varepsilon)a/3$ and $r_6 = (1 - 2\varepsilon)a/3$ with $2r_5 + r_6 = a$. r_5 is the length of edges between a hexagon and a pentagon (single bonds) and r_6 is the length of edges connecting two pentagons (double bond). That means, ε is a measure of the

Mathematica**GTBuckyBall, GTSymmetryElementQ**

```
In[8]:= r5 = 1.455; r6 = 1.391;
GTBuckyBall[r5, r6, GOCordinateSystem -> True, GOSphere -> False]
```



Out[8]=

Coordinates of the atoms in the cluster and check of symmetry.

```
In[10]:= c60 = GTBuckyBall[r5, r6, GOPlot -> False];
GTSymmetryElementQ[{C2x, C2y, C2z}, c60]
```

Out[11]= True

Figure 4.21 C_{60} molecule and check of some symmetry properties.

bond alteration. An ideal truncated icosahedron results from the construction if $\varepsilon = 0$ and $r_5 = r_6 = a/3$. Bond lengths measured within experiments [69, 70] are $r_6 = 1.391 \text{ \AA}$ and $r_5 = 1.445 \text{ \AA}$ ($\varepsilon \approx 0.015$).

The icosahedron group I consists of all rotations that leave the icosahedron invariant. To describe the additional symmetry elements necessary to build up the icosahedron groups in the same way as the point group elements (symbols, matrices) additional rotation axes have to be installed. **GTIcosahedronAxes** installs all additional axes for the construction of the groups I and I_h in agreement with Altmann and Herzog [71] (cf. Figure 4.22). The group I is constructed from two fivefold rotations, e.g., C_{51} and C_{53} . Afterwards, the group elements are transformed into symbolic form by **GTGetSymbol**. The group I_h is constructed as a direct product $I_h = I \otimes C_i$.

The buckyball consists of 20 hexagons and 12 pentagons. Therefore, the 120 symmetry elements of I_h are constructed from 12 fivefold axes through the pen-

GTIcosahedronAxes

```
In[8]:= GTIcosahedronAxes[GVerbose → False]
```

```
In[9]:= m1 = GTGetMatrix[C51]; m2 = GTGetMatrix[C53];
        grpim = GTGroupFromGenerators[{m1, m2}];
        qrpis = grpim // GTGetSymbol
```

Installation of I_h as a product group.

```
In[11]:= gcim = GTInstallGroup[Ci] // GTGetMatrix;
         grpihm = GTProductGroup[grpim, gcim];
         grpihs = grpihm // GTGetSymbol
```

direct product group

$$\text{Out}[12] = \left\{ \begin{array}{l} \text{IEe}, \text{C}_{2z}, \text{C}_{2y}, \text{IC}_{2x}, \text{C}_{2p}, \text{IC}_{5z}^2, \text{IC}_{51}, \text{C}_{3\beta}^1, \text{IC}_{5\kappa}^1, \text{C}_{2q}, \text{C}_{37}, \text{IC}_{52}, \text{IC}_{51}, \text{C}_{37}, \text{C}_{2o}, \\ \text{IC}_{5z}^3, \text{C}_{3\beta}, \text{IC}_{5z}^1, \text{IC}_{59}^2, \text{C}_{2r}, \text{IC}_{3\delta}, \text{C}_{3\beta}, \text{C}_{3y}, \text{IC}_{3\alpha}, \text{IC}_{3\beta}^1, \text{C}_{3y}^1, \text{C}_{3\beta}^1, \text{IC}_{3\beta}, \text{C}_{3\beta}^1, \text{IC}_{3\alpha}^1, \\ \text{IC}_{37}^1, \text{C}_{3\beta}^1, \text{C}_{3\alpha}, \text{IC}_{3y}, \text{IC}_{3\beta}, \text{C}_{3\delta}, \text{IC}_{2r}, \text{C}_{59}^2, \text{C}_{5z}^1, \text{IC}_{3\beta}, \text{C}_{59}^3, \text{IC}_{2o}, \text{IC}_{37}, \text{C}_{5z}^1, \text{C}_{52}, \\ \text{IC}_{37}^1, \text{IC}_{2q}, \text{C}_{5\kappa}^1, \text{IC}_{3\beta}^1, \text{C}_{51}, \text{C}_{5z}^2, \text{IC}_{2p}, \text{C}_{2x}, \text{IC}_{2y}, \text{IC}_{2z}, \text{Ee}, \text{C}_{2j}, \text{IC}_{5z}^1, \text{IC}_{3\beta}, \text{C}_{5z}^1, \\ \text{IC}_{5\kappa}, \text{C}_{2g}, \text{C}_{54}^1, \text{IC}_{3\lambda}, \text{IC}_{3\beta}^1, \text{C}_{54}^1, \text{C}_{2t}, \text{IC}_{59}^1, \text{C}_{53}^1, \text{IC}_{3\beta}^1, \text{IC}_{59}, \text{C}_{2\beta}, \text{IC}_{2n}, \text{C}_{36}, \text{C}_{52}^1, \\ \text{IC}_{53}, \text{C}_{3\beta}^1, \text{IC}_{2k}, \text{IC}_{54}, \text{C}_{5z}^1, \text{C}_{52}^1, \text{IC}_{54}^1, \text{IC}_{2m}, \text{C}_{3\kappa}, \text{IC}_{5\beta}^1, \text{C}_{5z}^1, \text{C}_{3\beta}^1, \text{IC}_{21}, \text{C}_{21}, \text{IC}_{3\beta}^1, \\ \text{IC}_{5z}^1, \text{C}_{53}, \text{IC}_{35}, \text{C}_{2m}, \text{C}_{54}^1, \text{IC}_{52}^1, \text{C}_{52}^1, \text{C}_{25}, \text{IC}_{3\beta}^1, \text{C}_{53}, \text{IC}_{5z}^1, \text{IC}_{36}, \text{C}_{2n}, \text{IC}_{2\beta}, \\ \text{C}_{59}, \text{C}_{3\beta}^1, \text{IC}_{53}^1, \text{C}_{59}, \text{IC}_{2t}, \text{IC}_{54}^1, \text{C}_{3\beta}^1, \text{C}_{3\lambda}, \text{IC}_{5z}^1, \text{IC}_{2g}, \text{C}_{5\kappa}, \text{IC}_{5z}^1, \text{C}_{3\beta}, \text{C}_{5\kappa}^1, \text{IC}_{2j} \end{array} \right.$$

```
In[13]:= r5 = 1.455; r6 = 1.391; c60 = GTBuckyBall[r5, r6, GOPlot -> False];  
GTSymmetryElementQ[grpihs, c60]
```

Out[14]= True

Figure 4.22 Installation of the groups I and I_h and symmetry properties of C_{60} .

tagons and 20 threefold axes through the hexagons. Additionally, 15 twofold axes exist through edges connecting hexagons. As demonstrated before, the three coordinate axes belong to this set. Furthermore, the structure reveals inversion symmetry.

Having installed the groups I and I_h in this way, all standard manipulations implemented within GTPack can be applied. The use of representation theory (as will be discussed in Chapter 5) is straightforward and GTPack can therefore be used to generate character tables and irreducible representations for I and I_h automatically (cf. [72–74]). This constitutes the basis for the discussion of the electronic structure of C_{60} [75–81].

5

Representation Theory

Ich kann es nun einmal nicht lassen, in diesem Drama von Mathematik und Physik, die sich im Dunkeln befruchten, aber von Angesicht zu Angesicht so gerne einander verkennen und verleugnen, die Rolle des (wie ich genugsam erfuhr, oft unerwünschten) Boten zu spielen.

Hermann Weyl
(*Gruppentheorie und Quantenmechanik*, 1928)

This chapter introduces matrix representations, i.e., homomorphic mappings of abstract groups to groups of square matrices. The behavior of the matrices under similarity transformations will lead to the concept of reducible and irreducible representations. Especially irreducible representations play an important role, e.g., in electronic structure theory each eigenstate of the Hamiltonian can be associated to a certain irreducible representation. By introducing the character of a group element (which is the trace of the representation matrix), it is shown that there is only a finite number of inequivalent irreducible representations for any finite group. The orthogonality theorem for irreducible representations is a central theorem in representation theory. The proof of the orthogonality theorem is based on the two lemmas of Schur. From the orthogonality theorem the orthogonality of the character system of the irreducible representations follows, which has important consequences, e.g. that the number of inequivalent irreducible representations is equal to the number of classes. The chapter continues with the introduction of basis functions, direct product representations and the WIGNER–ECKART theorem. Finally the theory of induced representations is outlined.

5.1

Definition of Matrix Representations

Matrix representations	
GTRegularRepresentation	Installs the regular representation of a finite group
GTAngularMomentumRep	Installs a matrix representation using WIGNER-D matrices

Up to now, the elements of a group have had an abstract structure, defined by their multiplication table. The idea of representation theory is to map the elements of an abstract group to transformations of vector spaces. An endomorphism of a finite vector space $\mathcal{V}$, i.e., a map $\phi : \mathcal{V} \rightarrow \mathcal{V}$, can be expressed via a square matrix. According to Definition 6, a homomorphism of a group $\mathcal{G}$ to a group of square matrices will preserve the group structure.

Definition 24 (Matrix representation, unitary representation). *A homomorphic map of a group $\mathcal{G}$ to a group of square matrices Γ with matrix multiplication as the group multiplication is called the matrix representation of the group $\mathcal{G}$. A matrix representation is called a unitary representation if all representation matrices are unitary matrices, i.e., $\underline{\Gamma}(T) \cdot \underline{\Gamma}(T)^\dagger = \underline{1}$.*

In the following, the short form *representation* will be used in the sense of matrix representations. Furthermore, all considered representations are unitary representations¹⁾. Let's consider a simple example using the point group C_3 with the elements E , C_{3z} and C_{3z}^{-1} , where C_{3z} describes a threefold rotation about the z -axis. Subsequently, two specific representations are discussed. The first, Γ_1 is given by the identity representation, where each element is mapped to the 1,

$$\underline{\Gamma}_1(E) = \underline{\Gamma}_1(C_{3z}) = \underline{\Gamma}_1(C_{3z}^{-1}) = 1. \quad (5.1)$$

The second, Γ_2 , is constructed by two-dimensional passive rotation matrices²⁾ as

$$\underline{\Gamma}_2(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \underline{\Gamma}_2(C_{3z}) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \quad (5.2)$$

and

$$\underline{\Gamma}_2(C_{3z}^{-1}) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}. \quad (5.3)$$

- 1) Sticking to unitary representations is not a restriction since as soon as the representation matrices have nonvanishing determinants they can be brought into unitary form by an equivalence (similarity) transformation [83].
- 2) Also, the 3-dimensional rotation matrices as discussed in Section 2.1 represent a valid matrix representation.

Table 5.1 Commands for the generation of matrix representations in GTPack and a classification of which kind of matrices are used. If the representation is faithful in general it

is denoted with +, and otherwise with –. In the last column a reference to a more detailed description within the book is given.

Module	Matrices	Faithful	Chapter
GTInstallGroup	Rotation matrices	+	3.1
GTTableToGroup	Permutation matrices	+	3.1
GTRegularRepresentation	Permutation matrices	+	5.1
GTAngularMomentumRep	WIGNER-D matrices	–	A, 7.3

Clearly, both representations fulfill the relation

$$\underline{\Gamma}_i(T) \cdot \underline{\Gamma}_i(T') = \underline{\Gamma}_i(TT'), \quad T, T' \in \mathcal{G}, \quad i = 1, 2. \quad (5.4)$$

Both sets Γ_1 and Γ_2 form a group and are valid matrix representations. However, the order of both groups differ, since $\text{ord}(\Gamma_1) = 1$ and $\text{ord}(\Gamma_2) = 3$. Furthermore, the map $\phi_2 : C_3 \rightarrow \Gamma_2$ is bijective (injective and surjective), the map $\phi_1 : C_3 \rightarrow \Gamma_1$ not.

Definition 25 (Faithful representation). *A (matrix) representation Γ of a group $\mathcal{G}$ is called faithful, if the homomorphism $\phi : \mathcal{G} \rightarrow \Gamma$ is bijective, in other words ϕ is an isomorphism.*

Definition 26 (Dimension of representations). *Consider a matrix representation Γ of a group $\mathcal{G}$, consisting of $l \times l$ -dimensional matrices $\underline{\Gamma}(T)$. Then l is called the dimension of the representation Γ .*

GTPack offers several ways for generating matrix representations. Not all of them are faithful. A list of the implemented commands can be found in Table 5.1. From the multiplication table of a group it is possible to construct the so-called regular representation.

Definition 27 (Regular representation). *For a given group $\mathcal{G}$ with elements $T_1, \dots, T_g \in \mathcal{G}$ and order $g = \text{ord}(\mathcal{G})$, the regular representation is defined by the $g \times g$ -dimensional matrices $\underline{\Gamma}^{\text{reg}}(T_1), \dots, \underline{\Gamma}^{\text{reg}}(T_g)$, given by*

$$\Gamma_{jk}^{\text{reg}}(T_i) = \begin{cases} 1 & \text{if } T_j(T_k)^{-1} = T_i \\ 0 & \text{otherwise} \end{cases}. \quad (5.5)$$

To verify that the regular representation is a valid matrix representation, it has to be shown that the map $\mathcal{G} \rightarrow \Gamma^{\text{reg}}$ is a homomorphism. The matrix product of two representation matrices $\underline{\Gamma}^{\text{reg}}(T_a)$ and $\underline{\Gamma}^{\text{reg}}(T_b)$ can be evaluated by

$$[\underline{\Gamma}^{\text{reg}}(T_a) \cdot \underline{\Gamma}^{\text{reg}}(T_b)]_{jk} = \sum_{m=1}^g \Gamma_{jm}^{\text{reg}}(T_a) \Gamma_{mk}^{\text{reg}}(T_b). \quad (5.6)$$

GTRegularRepresentation

First, the point group C_{4v} is installed.

```
In[9]:= c4v = GTInstallGroup[C4v, GVerbose -> False]
```

$$\text{Out[9]} = \left\{ \text{Ee}, C_{2z}, C_{4z}^{-1}, C_{4z}, IC_{2x}, IC_{2a}, IC_{2b}, IC_{2y} \right\}$$

The regular representation is obtained using `GTRegularRepresentation`.

```
In[10]:= Map[MatrixForm, GTRegularRepresentation[c4v]]
```

[illegible]

Figure 5.1 Installation of the regular representation of the point group C_{4v} using **GTRegular-Representation**.

Since there is only one nonzero element in every row as well as in every column for each representation matrix of I^{reg} , a single entry of the matrix product can only be nonzero if there exists an index m' such that $I_{jm'}^{\text{reg}}(T_a) = I_{m'k}^{\text{reg}}(T_b) = 1$. Hence, the sum can be evaluated as

$$\sum_{m=1}^g \Gamma_{jm}^{\text{reg}}(T_a) \Gamma_{mk}^{\text{reg}}(T_b) = \begin{cases} 1 & \text{if there is an } m': \Gamma_{jm'}^{\text{reg}}(T_a) = \Gamma_{m'k}^{\text{reg}}(T_b) = 1 \\ 0 & \text{otherwise} \end{cases}. \quad (5.7)$$

Furthermore, if $I_{jm'}^{\text{reg}}(T_a) = I_{m'k}^{\text{reg}}(T_b) = 1$, it can be concluded that $T_a = T_j(T_{m'})^{-1}$ and $T_b = T_{m'}(T_k)^{-1}$ and therefore $T_a T_b = T_j(T_{m'})^{-1} T_{m'}(T_k)^{-1} = T_j(T_k)^{-1}$. Thus,

(5.7) can be rewritten as

$$\sum_{m=1}^g \Gamma_{jm}^{\text{reg}}(T_a) \Gamma_{mk}^{\text{reg}}(T_b) = \begin{cases} 1 & \text{if } T_j(T_k)^{-1} = T_a T_b \\ 0 & \text{otherwise} \end{cases} . \quad (5.8)$$

From (5.8) it follows that

$$\underline{\underline{\Gamma}}^{\text{reg}}(T_a) \cdot \underline{\underline{\Gamma}}^{\text{reg}}(T_b) = \underline{\underline{\Gamma}}^{\text{reg}}(T_a T_b) . \quad (5.9)$$

Moreover, since there is only one unique element $T_i \in \mathcal{G}$ fulfilling the relation $T_j(T_k)^{-1} = T_i$ for fixed j and k , the regular representation is faithful.

Example 20 (The regular representation of C_{4v}). With the help of the command **GTRegularRepresentation** the regular representation of a finite group can be installed. An example for the point group C_{4v} is illustrated in Figure 5.1. After installing C_{4v} using **GTInstallGroup**, **GTRegularRepresentation** is evaluated. The regular representation is defined according to equation (5.5). Following (5.5), the first row of an element T_i is given by

$$\Gamma_{1k}^{\text{reg}}(T_i) = \begin{cases} 1 & \text{if } E(T_k)^{-1} = T_i \\ 0 & \text{otherwise} \end{cases} . \quad (5.10)$$

That means, the entry 1 occurs if T_k is the inverse element of T_i . Considering $T_i = C_{2z}$, the inverse element is C_{2z} itself. As C_{2z} is the second element within the list shown in Figure 5.1, a 1 occurs within the first row and second column of the representation matrix. Similarly, discussing $T_i = C_{4z}$, the inverse element is given by C_{4z}^{-1} . As C_{4z}^{-1} is the third element within the list, the representation matrix of C_{4z} contains a 1 in the first row and third column.

Task 13 (Matrix representation using rotation matrices). Use the *Mathematica* command **RotationMatrix** to form a matrix representation of the group

$$C_4 = \{Ee, C_{4a}, C_{2a}, C_{4a}^{-1}\} , \quad (5.11)$$

where the rotation axis is given by

$$\mathbf{e}_a = \left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0 \right) . \quad (5.12)$$

Keep in mind that there is an active and a passive definition of rotation matrices (see Section 2.1).

5.2

Reducible and Irreducible Representations

Matrix representations	
GTNumberOfreps	Gives the number of inequivalent irreducible representations
GTGetIrep	Installs an irreducible representation
GTIrepDimension	Gives the dimension of an irreducible representation
GTClebschGordanSum	Constructs the CLEBSCH–GORDAN sum of two matrix representations

In the following, the representations of groups will be classified. Consider a group $\mathcal{G}$ with elements T and a block diagonal unitary matrix representation Γ with matrices $\underline{\underline{\Gamma}}(T)$,

$$\underline{\underline{\Gamma}}(T) = \begin{pmatrix} \underline{\underline{\Gamma}}^1(T) & 0 \\ 0 & \underline{\underline{\Gamma}}^2(T) \end{pmatrix}, \quad (5.13)$$

where the matrix elements are given by an $m \times m$ matrix $\underline{\underline{\Gamma}}^1(T) \in \Gamma^1$ as well as an $n \times n$ matrix $\underline{\underline{\Gamma}}^2(T) \in \Gamma^2$ ³⁾. For a second element $\underline{\underline{\Gamma}}(T') \in \Gamma$ it follows by definition of a matrix representation,

$$\underline{\underline{\Gamma}}(T)\underline{\underline{\Gamma}}(T') = \underline{\underline{\Gamma}}(TT'). \quad (5.14)$$

Since Γ is block diagonal, the multiplication implies that Γ^1 and Γ^2 have to be matrix representations of $\mathcal{G}$ as well,

$$\begin{aligned} \underline{\underline{\Gamma}}(T)\underline{\underline{\Gamma}}(T') &= \begin{pmatrix} \underline{\underline{\Gamma}}^1(T)\underline{\underline{\Gamma}}^1(T') & 0 \\ 0 & \underline{\underline{\Gamma}}^2(T)\underline{\underline{\Gamma}}^2(T') \end{pmatrix} \\ &= \underline{\underline{\Gamma}}(TT') \\ &= \begin{pmatrix} \underline{\underline{\Gamma}}^1(TT') & 0 \\ 0 & \underline{\underline{\Gamma}}^2(TT') \end{pmatrix}. \end{aligned} \quad (5.15)$$

Two matrices $\underline{\underline{A}}$ and $\underline{\underline{B}}$ are called *similar*, if there exists a non-singular square matrix $\underline{\underline{S}}$, such that

$$\underline{\underline{S}}\underline{\underline{A}}\underline{\underline{S}}^{-1} = \underline{\underline{B}}. \quad (5.16)$$

The transformation in (5.16) is called the *similarity transformation*.

3) As an example one can think of the group C_3 and the two representations introduced at the beginning of the previous section.

Theorem 13 (Similarity transformations of representations). *Let $\mathcal{G}$ be a group, Γ a l -dimensional representation of $\mathcal{G}$, and $\underline{\underline{S}}$ a $l \times l$ -dimensional non-singular matrix. Then, the set $\tilde{\Gamma}$ with matrices*

$$\tilde{\Gamma}(T) = \underline{\underline{S}} \Gamma(T) \underline{\underline{S}}^{-1}, \quad T \in \mathcal{G}, \quad \Gamma(T) \in \Gamma, \quad (5.17)$$

is a matrix representation of $\mathcal{G}$.

Proof. The theorem can be shown by verifying that $\tilde{\Gamma}$ preserves the group structure of $\mathcal{G}$,

$$\begin{aligned} \tilde{\Gamma}(T) \tilde{\Gamma}(T') &= \underline{\underline{S}} \Gamma(T) \underline{\underline{S}}^{-1} \underline{\underline{S}} \Gamma(T') \underline{\underline{S}}^{-1} \\ &= \underline{\underline{S}} \Gamma(T) \Gamma(T') \underline{\underline{S}}^{-1} \\ &= \underline{\underline{S}} \Gamma(TT') \underline{\underline{S}}^{-1} \\ &= \tilde{\Gamma}(TT'). \end{aligned} \quad (5.18)$$

□

The representations Γ and $\tilde{\Gamma}$ are said to be *similar* or *equivalent*.

Definition 28 (Reducible representation). *Consider a unitary matrix representation Γ of a finite group $\mathcal{G}$ with elements $\underline{\underline{\Gamma}}(T)$. The representation is said to be reducible if there exists a similarity transformation to a block diagonal form*

$$\underline{\underline{S}} \underline{\underline{\Gamma}}(T) \underline{\underline{S}}^{-1} = \begin{pmatrix} \underline{\underline{\Gamma}}^1(T) & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \cdots & \underline{\underline{\Gamma}}^p(T) \end{pmatrix}, \quad (5.19)$$

for all elements $T \in \mathcal{G}$.

In Section 5.5, the elements of the transformation matrix $\underline{\underline{S}}$ will be identified as CLEBSCH–GORDAN coefficients. In general, not every matrix representation can be block diagonalized.

Definition 29 (Irreducible representation). *If a matrix representation Γ of a group $\mathcal{G}$ with elements $\underline{\underline{\Gamma}}(T)$ cannot be transformed to a block diagonal form, it is said to be an irreducible representation of the group $\mathcal{G}$.*

Every reducible representation can be transformed to a block diagonal form, containing irreducible representation matrices $\underline{\underline{\Gamma}}^1(T) \dots \underline{\underline{\Gamma}}^p(T)$ on the diagonal. It is common to introduce the notation

$$\underline{\underline{S}} \underline{\underline{\Gamma}} \underline{\underline{S}}^{-1} = \Gamma^1 \oplus \cdots \oplus \Gamma^p \quad \text{or} \quad \Gamma \simeq \Gamma^1 \oplus \cdots \oplus \Gamma^p. \quad (5.20)$$

Matrix representations linked by the operator $\oplus$ form the so-called CLEBSCH–GORDAN *sum*.

Example 21 (Installation of irreducible representations). As an example, two irreducible representations of the point group O will be installed using the command **GTGetIrep**⁴⁾. The point group O has five inequivalent irreducible representations, as can be verified using **GTNumberOfIreps**⁵⁾. Two of them are one-dimensional, one is two-dimensional, and the other two are three-dimensional. For the calculation of the matrices of a certain irreducible representation **GTGetIrep** needs the installed point group, and the index of the desired irreducible representation (in the present case a number between 1 and 5). The output of **GTGetIrep** is a list of representation matrices, where the matrices are ordered according to the group elements of the given point group. After installing an irreducible representation the dimension can be estimated by means of **GTIrepDimension**. The usage of **GTNumberOfIreps**, **GTGetIrep**, and **GTIrepDimension** is illustrated in Figure 5.2.

Example 22 (CLEBSCH–GORDAN sum). Referring to the previous example it is shown, how to calculate the CLEBSCH–GORDAN sum of two (irreducible) representations. Figure 5.2 illustrates how to install the first and the third irreducible representation of the cubic point group O using **GTGetIrep**. By means of **GTClebschGordanSum** the CLEBSCH–GORDAN sum of the two irreducible representations can be constructed. As input the lists of the representation matrices of the two representations are needed. The *Mathematica* code of the example can be found in Figure 5.3. The operator $\oplus$ can be used as an alternative to the command **GTClebschGordanSum**⁶⁾.

Task 14 (Reducible representations). Repeat Task 13 choosing $\mathbf{e}_z = (0, 0, 1)$ as the main rotation axis for the group C_4 ,

$$C'_4 = \{Ee, C_{4z}, C_{2z}, C_{4z}^{-1}\}. \quad (5.21)$$

The representation now becomes block diagonal. Is it a reducible representation? What is the transformation matrix connecting C_4 of Task 13 with C'_4 ?

5.2.1

The Orthogonality Theorem for Irreducible Representations

The orthogonality theorem for irreducible representations is a central theorem in representation theory. The proof of the orthogonality theorem⁷⁾ is based on the two lemmas of SCHUR.

4) Within **GTGetIrep** the algorithm of FLODMARK and BLOKKER [84, 85] is used.
5) It will be shown in Section 5.3.1 that the number of inequivalent irreducible representations is equal to the number of classes.

6) Within *Mathematica* the operator $\oplus$ can be generated by `\[CirclePlus]` or by typing the sequence ESC c+ ESC.

7) See DRESSELHAUS *et al.* [83] or ARTIN [86].

GTNumberOfReps, GTGetRep, GTRepDimension

```
In[9]:= o = GTInstallGroup[0, GVerbose → False]
```

Using `GTNumberOfReps` it can be estimated how many inequivalent irreducible representations exist.

The given group has 5 non-equivalent irreducible representations.

As an example the representations Γ^1 and Γ^3 are installed.

```
In[12]:= Map[MatrixForm, Irep1]
```

```
In[13]:= GTIrepDimension[Irep1]
```

```
In[14]:= Irep3 = GTGetIrep[o, 3];
```

```
In[15]:= Map[MatrixForm, Irep3]
```

```
In[16]:= GTrepDimension[Irep3]
```

Out[16]= 2

Figure 5.2 Installation of irreducible representations of the point group O using **GTGetIrep**.

Theorem 14 (First lemma of SCHUR). *Let Γ be a l -dimensional matrix representation of a group G and $\underline{A}$ a non-singular $l \times l$ matrix. If $\underline{A}$ commutes with all representation matrices $\underline{\Gamma}(T) \in \Gamma$, then one of the following two cases has to be true,*

- I. Γ is irreducible $\Rightarrow \underline{\underline{A}}$ is a multiple of the identity matrix $\underline{\underline{A}} = \lambda \underline{\underline{1}}$.
- II. $\underline{\underline{A}}$ is not a multiple of the identity matrix $\Rightarrow \Gamma$ is reducible.

Mathematica**GTClebschGordanSum**

```
In[17]:= GTClebschGordanSum[Irep1, Irep3];
```

```
In[18]:= Map[MatrixForm, %]
```

$$\text{Out[18]} = \left\{ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \right.$$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix},$$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix},$$

$$\left. \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} \right\}$$

Figure 5.3 Calculation of the CLEBSCH–GORDAN sum of two irreducible representations of the point group O using **GTClebschGordanSum**. The irreducible representations irep1 and irep3 were calculated in Example 21.

Whereas the first lemma of SCHUR gives a strong statement about the irreducibility of a l -dimensional representation from the commutation of the representation matrices with a $l \times l$ -dimensional square matrix, the second lemma of SCHUR discusses the transformation with general $l_1 \times l_2$ -dimensional matrices.

Theorem 15 (Second lemma of SCHUR). *Let Γ^1 and Γ^2 be two irreducible matrix representations of a group $\mathcal{G}$ with dimensions l_1 and l_2 . If there is a $l_1 \times l_2$ -dimensional matrix $\underline{\underline{M}}$ with the property*

$$\underline{\underline{\Gamma}}^1(T) \underline{\underline{M}} = \underline{\underline{M}} \underline{\underline{\Gamma}}^2(T) \quad (5.22)$$

for all $T \in \mathcal{G}$, then one of the following cases has to be true

- I. $l_1 \neq l_2 \Rightarrow \underline{\underline{M}} = 0$
- II. $l_1 = l_2$ and $\underline{\underline{M}} \neq 0 \Rightarrow \Gamma^1 \sim \Gamma^2$

In the orthogonality theorem the dot product of two vectors of length g is calculated. The vectors are formed from elements of the representation matrices of each $T \in \mathcal{G}$ for a representation Γ^p .

Theorem 16 (Orthogonality theorem for irreducible representations). *Consider a group G with elements T as well as two unitary irreducible representations Γ^p and Γ^q . Let g denote the order of the group G and l_p the dimension of the representation matrices of Γ^p , then the following relation holds*

$$\sum_{T \in G} \Gamma_{\mu\nu}^p(T) \left[\Gamma_{\mu'\nu'}^q(T) \right]^* = \frac{g}{l_p} \delta_{p,q} \delta_{\mu,\mu'} \delta_{\nu,\nu'} . \quad (5.23)$$

Example 23 (Orthogonality theorem). As an alternative to a mathematical proof of the orthogonality theorem⁸⁾ the following example using the point group C_{3v} is given to verify the correctness (see Figure 5.4). The group C_{3v} has six elements and it is possible to construct three inequivalent irreducible representations, as can be verified with **GTNumberOfIreps**. Two of the irreducible representations are one-dimensional representations and the third one is a two-dimensional representation. After installing the irreducible representations using **GTGetIrep** a summation according to equation (5.23) is performed. As can be seen in Figure 5.4 the orthogonality of the irreducible representations is clearly revealed.

Mathematica

```

At first, the point group  $C_{3v}$  is installed. Afterwards, the number of irreducible representations and the
group order is computed.

In[9]:= c3v = GTInstallGroup[C3v, GOverbose -> False];
noi = GTNumberOfIreps[c3v];
g = GTGroupOrder[c3v];

The given group has 3 non-equivalent irreducible representations.

Order of the group: 6

All irreducible representations are installed using GTGetIrep.

In[12]:= Ireps = Table[GTGetIrep[c3v, i], {i, 1, noi}];

Finally, summations according to the orthogonality theorem are performed.

In[13]:= erg = Table[
  Table[
    Table[
       $\mu = 1;$ 
       $\mu s = 1;$ 
      Sum[Ireps[[p, T, v,  $\mu$ ]] Conjugate[Ireps[[q, T, vs,  $\mu s$ ]]], {T, 1, g}] *
      Tr[Ireps[[p, 1]]] / g,
      {v, 1, Length[Ireps[[p, 1]]]},
      {vs, 1, Length[Ireps[[q, 1]]]} // Transpose // TableForm,
      {q, 1, noi}],
      {p, 1, noi}] // Simplify;

In[14]:= TableForm[erg, TableHeadings -> {{{" $\Gamma 1$ ", " $\Gamma 2$ ", " $\Gamma 3$ "}, {" $\Gamma 1$ ", " $\Gamma 2$ ", " $\Gamma 3$ "}}}
Out[14]//TableForm=

```

	$\Gamma 1$	$\Gamma 2$	$\Gamma 3$
$\Gamma 1$	1	0	0
$\Gamma 2$	0	1	0
$\Gamma 3$	0	0	1

Figure 5.4 Verifying the orthogonality theorem for the point group C_{3v} .

8) See CORNWELL [36] or DRESSELHAUS *et al.* [83].

5.3

Characters and Character Tables

Character tables	
GTCharacterTable	Calculates the character table of a finite group
GTlrep	Calculates the number of times an irreducible representation occurs within a reducible representation

Two equivalent representations are related to each other by a similarity transformation of the representation matrices. In the following, two questions will be addressed. First, how to identify two representations being inequivalent, and second, how many inequivalent irreducible representations can be found for a given finite group. To characterize a matrix representation, a quantity is needed that is invariant under similarity transformations.

Definition 30 (Character). *Let Γ be a l -dimensional matrix representation of a group $\mathcal{G}$ with representation matrices $\underline{\Gamma}(T)$ for each element $T \in \mathcal{G}$. The character of $\underline{\Gamma}(T)$ is defined as*

$$\chi(T) = \text{Tr}(\underline{\Gamma}(T)) = \sum_{i=1}^l \underline{\Gamma}_{ii}(T). \quad (5.24)$$

The set of all characters of a matrix representation is called the *character system*. Since the character of a matrix representation is invariant under similarity transformations, two representations are equivalent if they have the same character system. The character of the matrix representation of the identity element is given by the dimension of the representation matrix, since it is represented by the identity matrix. However, also the calculation of characters for all other elements can be simplified, since the elements within a certain conjugacy class share the same character.

Theorem 17 (Characters of elements in one class). *Let Γ be a representation of the group $\mathcal{G}$ with elements $T \in \mathcal{G}$, then all elements within a class share the same character.*

Proof. Suppose $S, T \in \mathcal{G}$ are two elements of the same conjugacy class, then there exists an element $X \in \mathcal{G}$ such that

$$S = XTX^{-1}, \quad (5.25)$$

and

$$\underline{\Gamma}(S) = \underline{\Gamma}(X) \underline{\Gamma}(T) \underline{\Gamma}(X)^{-1}. \quad (5.26)$$

Since $\underline{\Gamma}(X)$ is a non-singular matrix, the trace is preserved and

$$\chi(S) = \text{Tr } \underline{\Gamma}(S) = \text{Tr } [\underline{\Gamma}(X) \underline{\Gamma}(T) \underline{\Gamma}(X)^{-1}] = \text{Tr } \underline{\Gamma}(T) = \chi(T). \quad (5.27)$$

□

Every finite group has a finite number N of irreducible representations, as will be explained subsequently in Section 5.3.1. The characters $\chi^i(T)$ of the elements of the irreducible representations $\Gamma^1, \dots, \Gamma^N$ play an important role, since for every reducible representation the characters can be constructed as a linear combination of the $\chi^i(T)$.

Theorem 18 (The characters of a reducible representation). *Let Γ be a unitary reducible representation of the group $\mathcal{G}$ and N the number of inequivalent irreducible representations. Suppose that each irreducible representation Γ^p occurs n_p times in Γ , then the character of the representation matrix $\underline{\Gamma}(T)$ is given by*

$$\chi(T) = \sum_{p=1}^N n_p \chi^p(T). \quad (5.28)$$

Proof. If Γ is reducible and N is the number of inequivalent irreducible representations, then there exists a matrix $\underline{S}$ that transforms each matrix $\underline{\Gamma}(T)$ into a block form consisting of M matrices on the main diagonal. Each of the M matrices is associated with one of the N irreducible representations Γ^p . Since the trace is preserved under similarity transformations, it follows that

$$\chi(T) = \text{Tr } (\underline{S} \underline{\Gamma}(T) \underline{S}^{-1}) = \text{Tr } \begin{pmatrix} \underline{\Gamma}^{p_1}(T) & \dots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \dots & \underline{\Gamma}^{p_M}(T) \end{pmatrix}. \quad (5.29)$$

Each irreducible representation Γ^p occurs n_p times within this block form. Hence, the trace, i.e., the character, is given by

$$\chi(T) = n_1 \chi^1(T) + \dots + n_N \chi^N(T) = \sum_{p=1}^N n_p \chi^p(T).$$

□

Example 24 (Characters of the regular representation). In Definition 27, the regular representation Γ^{reg} of a group $\mathcal{G}$ with dimension g was introduced via

$$\Gamma_{jk}^{\text{reg}}(T_i) = \begin{cases} 1 & \text{if } T_j(T_k)^{-1} = T_i \\ 0 & \text{otherwise} \end{cases}. \quad (5.30)$$

Mathematica**GTRegularRepresentation**

With the help of `GTInstallGroup`, the point group C_{4v} is installed.

```
In[9]:= c4v = GTInstallGroup[C4v, GOverbose -> False]
```

```
Out[9]:= {Ee, C2z, C4z^-1, C4z, IC2x, IC2a, IC2b, IC2y}
```

The characters or traces of the regular representation matrices are given by:

```
In[10]:= Map[Tr, GTRegularRepresentation[c4v]]
```

```
Out[10]:= {8, 0, 0, 0, 0, 0, 0, 0}
```

Figure 5.5 Calculation of the characters of the regular representation of the point group C_{4v} .

The identity element of Γ^{reg} is given by the $g \times g$ -dimensional identity matrix $\underline{1}_g$ and therefore, its character is given by

$$\chi^{\text{reg}}(E) = g. \quad (5.31)$$

For the regular representation, the diagonal elements of the representation matrix of an element $T_i \in G$ are 1 if $T_j (T_j)^{-1} = T_i$ and 0 otherwise. However, the product of a group element with its inverse always gives the identity element. Therefore, the diagonal elements of the representation matrices are 0 for all $T_i \neq E$. Since the character of an element is given by the trace of the representation matrix (i.e., the sum over the diagonal elements), it follows that

$$\chi^{\text{reg}}(T) = 0, \quad \text{for all } T \neq E. \quad (5.32)$$

The statement can be verified using the point group C_{4v} , where the regular representation is installed using **GTRegularRepresentation** (see Figure 5.5). Calculating the trace of the representation matrices gives $\chi^{\text{reg}}(E) = 8$ for the identity and $\chi^{\text{reg}}(T) = 0$ for all other group elements.

Task 15 (Characters of a matrix representation). Go back to Task 13 and Task 14 and calculate the characters of the elements as the trace of the representation matrices. Are the results the same for C_4 and C'_4 ?

5.3.1

The Orthogonality Theorem for Characters

As a result of the orthogonality theorem for irreducible representations (Theorem 16), an orthogonality theorem for the characters of irreducible representations can be derived. A consequence of the character orthogonality theorem is that the number of irreducible representations of finite groups are also finite and equal to the number of classes of the group.

Theorem 19 (Orthogonality theorem for characters). *For the characters $\chi^p(T)$ and $\chi^q(T)$ of two irreducible representations Γ^p and Γ^q of a group $\mathcal{G}$ with elements $T \in \mathcal{G}$, the following orthogonality relation holds*

$$\sum_{T \in \mathcal{G}} \chi^p(T) [\chi^q(T)]^* = g \delta_{p,q}.$$

Proof. To prove the orthogonality theorem for characters the orthogonality theorem for irreducible representations (Theorem 16) is formulated for the diagonal elements of the representation matrices,

$$\sum_{T \in \mathcal{G}} \Gamma_{\mu\mu}^p(T) [\Gamma_{\nu\nu}^q(T)]^* = \frac{g}{l_p} \delta_{p,q} \delta_{\mu,\nu} \delta_{\mu,\nu}. \quad (5.33)$$

A summation over all μ and ν gives

$$\underbrace{\sum_{T \in \mathcal{G}} \sum_{\mu=1}^{l_p} \Gamma_{\mu\mu}^p(T)}_{\chi^p(T)} \underbrace{\sum_{\nu=1}^{l_q} [\Gamma_{\nu\nu}^q(T)]^*}_{[\chi^q(T)]^*} = \frac{g}{l_p} \delta_{p,q} \underbrace{\sum_{\mu=1}^{l_p} \sum_{\nu=1}^{l_q} \delta_{\mu,\nu} \delta_{\mu,\nu}}_{\delta_{\mu,\mu}}. \quad (5.34)$$

After using the definition of the character on the left-hand side of the equation, the right-hand side of the equation above can be evaluated to get

$$\sum_{T \in \mathcal{G}} \chi^p(T) [\chi^q(T)]^* = \frac{g}{l_p} \delta_{p,q} \underbrace{\sum_{\mu=1}^{l_p} \delta_{\mu,\mu}}_{l_p} = g \delta_{p,q}. \quad \square$$

According to Theorem 17, the elements within one conjugacy class have the same character. For a finite group $\mathcal{G}$ with N classes the characters can be seen as an N -dimensional vector within a certain vector space.

Theorem 20 (Number of irreducible representations). *For each finite group $\mathcal{G}$, the number of inequivalent irreducible representations is equal to the number of classes.*

Proof. Suppose that the group $\mathcal{G}$ has N different classes C_i containing n_i elements. Taking into account that the characters of all elements in one class are equal, the orthogonality theorem for characters can be rewritten as

$$\sum_{i=1}^N n_i \chi^p(C_i) [\chi^q(C_i)]^* = g \delta_{p,q}. \quad (5.35)$$

Introducing the vectors χ^p and χ^q according to

$$\chi^p = \sqrt{\frac{1}{g}} \begin{pmatrix} \sqrt{n_1} \chi^p(C_1) \\ \dots \\ \sqrt{n_N} \chi^p(C_N) \end{pmatrix}, \quad (5.36)$$

equation (5.35) can be understood as an orthogonality relation in an N -dimensional vector space,

$$\chi^p \cdot \chi^q = \delta_{p,q} . \quad (5.37)$$

Since an N -dimensional vector space has at most N linear independent orthogonal vectors, there are exactly N inequivalent irreducible representations. $\square$

5.3.2

Character Tables

A common way to illustrate the character system of a group is given by the character table, where the characters for each class and each irreducible representation are listed. Usually, the classes are listed at the top and the irreducible representations at the left-hand side of the table. According to Theorem 20 of the last section, the number of inequivalent irreducible representations is equal to the number of classes. Hence, the character table is square.

In general, the highest possible dimension of an irreducible representation of one of the 32 crystallographic point groups is three. As a consequence, for example, impurity states with degeneracy greater than three (e.g., angular momentum quantum number $l \geq 2$) have to split within a crystal field as will be shown in Chapter 7. Higher dimensions can occur if spin–orbit coupling is included or if non-crystallographic groups are present (e.g., the fullerene molecule C_{60} with icosahedral symmetry). The following example will explain the calculation of the character table with the help of GTPack.

Example 25 (The character table of D_{2h}). Within GTPack the character table can be calculated using `GTCharacterTable`⁹⁾. An example for the point group D_{2h} can be found in Figure 5.6. D_{2h} has the group order 8 and is an Abelian group. The last argument can be verified regarding the conjugacy classes, where each element forms a class on its own. Since D_{2h} has eight classes it also has to have eight irreducible representations (according to Theorem 20). Each irreducible representation is 1-dimensional as can be verified from the character of the identity element.

Task 16 (Character table of T_d). Calculate the character table of the point group T_d .

5.3.3

Notations of Irreducible Representations

A variety of different notations for irreducible representations were introduced during the past century. Within GTPack it is possible to choose between three of

9) Within the command `GTCharacterTable` the BURNSIDE algorithm is implemented. Details of the algorithm can be found in the book of HOLT *et al.* [87].

Mathematica**GTCharacterTable**

```
In[9]:= d2h = GTInstallGroup[D2h, GVerbose -> False]
```

```
Out[9]:= {Ee, C2f, C2e, C2x, IEe, IC2x, IC2e, IC2f}
```

After installing the point group using GTInstallGroup, GTCharacterTable is applied to calculate the character table.

```
In[10]:= GTCharacterTable[d2h]
```

	Ee	IEe	C _{2f}	C _{2e}	IC _{2x}	C _{2x}	IC _{2e}	IC _{2f}
Γ^1	1	1	1	1	1	1	1	1
Γ^2	1	-1	-1	-1	-1	1	1	1
Γ^3	1	-1	-1	1	1	-1	-1	1
Γ^4	1	-1	1	-1	1	-1	1	-1
Γ^5	1	-1	1	1	-1	1	-1	-1
Γ^6	1	1	-1	-1	1	1	-1	-1
Γ^7	1	1	-1	1	-1	-1	1	-1
Γ^8	1	1	1	-1	-1	-1	-1	1

$C_1 = \{Ee\}$

$C_2 = \{IEe\}$

$C_3 = \{C_{2f}\}$

$C_4 = \{C_{2e}\}$

$C_5 = \{IC_{2x}\}$

$C_6 = \{C_{2x}\}$

$C_7 = \{IC_{2e}\}$

$C_8 = \{IC_{2f}\}$

```
Out[10]:= {{ {Ee}, {IEe}, {C2f}, {C2e}, {IC2x}, {C2x}, {IC2e}, {IC2f}},
  {{1, 1, 1, 1, 1, 1, 1, 1}, {1, -1, -1, -1, -1, 1, 1, 1}, {1, -1, -1, 1, 1, -1, -1, 1},
  {1, -1, 1, -1, 1, -1, 1, -1}, {1, -1, 1, 1, -1, 1, -1, -1},
  {1, 1, -1, -1, 1, 1, -1, -1}, {1, 1, -1, 1, -1, -1, 1, -1},
  {1, 1, 1, -1, -1, -1, -1, 1}}, {{ $\Gamma^1$ ,  $\Gamma^2$ ,  $\Gamma^3$ ,  $\Gamma^4$ ,  $\Gamma^5$ ,  $\Gamma^6$ ,  $\Gamma^7$ ,  $\Gamma^8$ }}
```

Figure 5.6 The character table of the point group D_{2h} calculated using GTCharacterTable.

them, as will be explained in the following. The first notation is referred to as the BETHE notation, where the irreducible representations are labeled with increasing indices, $\Gamma^1, \Gamma^2, \dots$. Even though it is called BETHE notation, the labeling is arbitrary and does not refer to BETHE's original work of the year 1929 [88]. The second implemented denotation is called the BOUCKAERT notation. The BOUCKAERT notation is widely used within the solid-state community and is based on the paper of BOUCKAERT, SMOLUCHOWSKI, and WIGNER in the year 1936 [89].

The third implemented notation is called the MULLIKEN notation, which is widely used in quantum chemistry. In his paper of the year 1955, MULLIKEN summarized the different and sometimes deviating notations used in spectroscopy

and suggested a well-understandable standard notation [90]¹⁰. Because of the physical meaning of the notation of the irreducible representations, the MULLIKEN notation [71, 92] is explained in more detail in the following. The basic symbols are given by the characters A , B , E , T , F , H , and I , which denote the dimension of the irreducible representation.

- A singly degenerate representation; symmetrical with respect to rotation about the principal axis,
- B singly degenerate representation; antisymmetrical with respect to rotation about the principal axis,
- E **either**: doubly degenerate representation,
or: one of a pair of singly degenerate conjugate representations,
- T triply degenerate representation,
- F **either**: fourfold degenerate representation,
or: one of a pair of doubly degenerate conjugate representations,
- H fivefold degenerate representation,
- I sixfold degenerate representation.

To distinguish between an even and an odd transformation behavior of basis functions (see Section 5.4) under inversion, the subscripts g and u are introduced.

- Γ_g the representation is symmetrical with respect to inversion,
- Γ_u the representation is antisymmetrical with respect to inversion.

For axial groups (groups with a principal axis) with a horizontal mirror plane, the symmetry of the representation is labeled with a prime or double prime.

- Γ' the representation is symmetrical under reflection on a horizontal mirror plane,
- Γ'' the representation is antisymmetrical under reflection on a horizontal mirror plane.

For groups containing conjugate representations, superscripts are used.

- Γ^i $i = 1, 2$; the index distinguishes between two conjugate representations.

To distinguish between representations with similar notation, subscripts of integers are used. The index 1 always indicates the most symmetrical representation of A . Thus, A_1 denotes the totally symmetrical representation ($\Gamma(T) = 1, \forall T \in G$).

- Γ_i subscripts are used for indicating representations with similar properties. Half-integral indices ($1/2, 3/2$) are used for double group representations.

10) His original work was published without naming MULLIKEN as the author of the paper. An erratum in the following volume at the beginning of the year 1956 explains: "*The name of the writer was inadvertently omitted when this Report was published*" [91].

Example 26 (Notation of irreducible representations). As an example the character table of the point group O_h is calculated. Within the command **GTCharacterTable** the option **GOIrepNotation**¹¹⁾ can be specified to decide which notation should be used. The possible options are “Bethe,” “Mulliken,” or “Bouckaert.” Within Figure 5.7 the MULLIKEN notation is used to label the irreducible representations. As can be verified the point group O_h has four 1-dimensional representations ($A_{1g}, A_{2g}, A_{1u}, A_{2u}$), two 2-dimensional representations (E_g, E_u), and four 3-dimensional representations ($T_{1g}, T_{2g}, T_{1u}, T_{2u}$). By choosing **GOIrep-**

Mathematica

GTCharacterTable, GOIrepNotation

```
In[9]:= oh = GTInstallGroup[Oh, GOverbose -> False];
```

By specifying the option **GOIrepNotation** in **GTCharacterTable** the Mulliken notation can be used.

```
In[10]:= characterTable = GTCharacterTable[oh, GOIrepNotation -> "Mulliken"];
```

	Ee	3 C _{2z}	3 IC _{2x}	6 C _{2f}	6 IC _{4x} ⁻¹	6 IC _{2a}	6 C _{4z}	8 IC _{3b} ⁻¹	8 C _{3b} ¹	IEe
A _{1g}	1	1	1	1	1	1	1	1	1	1
A _{2u}	1	1	-1	-1	1	1	-1	-1	1	-1
A _{1u}	1	1	-1	1	-1	-1	1	-1	1	-1
A _{2g}	1	1	1	-1	-1	-1	-1	1	1	1
E _u	2	2	-2	0	0	0	0	1	-1	-2
E _g	2	2	2	0	0	0	0	-1	-1	2
T _{1g}	3	-1	-1	-1	1	-1	1	0	0	3
T _{2g}	3	-1	-1	1	-1	1	-1	0	0	3
T _{1u}	3	-1	1	-1	-1	1	1	0	0	-3
T _{2u}	3	-1	1	1	1	-1	-1	0	0	-3

$$C_1 = \{Ee\}$$

$$C_2 = \{C_{2z}, C_{2y}, C_{2x}\}$$

$$C_3 = \{IC_{2x}, IC_{2y}, IC_{2z}\}$$

$$C_4 = \{C_{2f}, C_{2e}, C_{2b}, C_{2d}, C_{2c}, C_{2a}\}$$

$$C_5 = \{IC_{4x}^{-1}, IC_{4x}, IC_{4z}^{-1}, IC_{4y}, IC_{4y}^{-1}, IC_{4z}\}$$

$$C_6 = \{IC_{2a}, IC_{2c}, IC_{2d}, IC_{2b}, IC_{2e}, IC_{2f}\}$$

$$C_7 = \{C_{4z}, C_{4y}^{-1}, C_{4y}, C_{4z}^{-1}, C_{4x}, C_{4x}^{-1}\}$$

$$C_8 = \{IC_{3b}^{-1}, IC_{3a}^{-1}, IC_{3b}, IC_{3b}, IC_{3a}, IC_{3y}, IC_{3y}^{-1}, IC_{3b}\}$$

$$C_9 = \{C_{3b}^{-1}, C_{3y}^{-1}, C_{3y}, C_{3a}, C_{3b}, C_{3b}, C_{3a}^{-1}, C_{3b}^{-1}\}$$

$$C_{10} = \{IEe\}$$

Figure 5.7 The character table of the point group O_h calculated using **GTCharacterTable**. For the denotation of the irreducible representations the MULLIKEN notation is used [90].

11) Within GTPack, deviations in the notation of irreducible representations can occur in comparison to other references, especially if nonstandard principle axes are used for the installation of the point groups.

Table 5.2 Comparison of BOUCKAERT notation and MULLIKEN notation for the irreducible representations of the point group O_h .

Mulliken	A_{1g}	A_{2g}	A_{1u}	A_{2u}	E_g	E_u	T_{1g}	T_{2g}	T_{1u}	T_{2u}
Bouckaert	1	2	1'	2'	12	12'	15'	25'	15	25

Notation—“Bouckaert”, the irreducible representations are labeled according to the BOUCKAERT notation. A comparison of the MULLIKEN notation and the BOUCKAERT notation can be found in Table 5.2. For denotation of the irreducible representation in electronic band structure calculations, the BOUCKAERT notation is often preferred. Alternative notations for irreducible representations have been suggested e.g., by HOWARTH and JONES [93] and by BELL [94].

Task 17 (Notations of irreducible representations). Reproduce the result of Table 5.2 in Example 26, i.e., calculate the character table of the point group O_h and switch the notation of irreducible representations by setting **GOIrepNotation** to “Bethe,” “Mulliken,” and “Bouckaert.”

5.3.4

Decomposition of Reducible Representations

In practice, a constructed representation is not necessarily irreducible. The decomposition in terms of irreducible representations is often desirable. Also, discussing systems under the influence of symmetry breaking perturbations often leads to the situation, that representations that are irreducible for a given group become reducible if the symmetry is reduced to a subgroup. As irreducible representations are associated to specific energy levels, such perturbations induce the splitting of these levels. More information about the correspondence between energy levels and irreducible representations will be given in Chapter 7.

Theorem 21 (Number of times Γ^p occurs in Γ). *The number of times n_p an irreducible representation Γ^p occurs within a reducible representation Γ of a group G with elements $T \in G$ can be calculated by*

$$n_p = \frac{1}{g} \sum_{T \in G} [\chi^p(T)]^* \chi(T), \quad (5.38)$$

where $\chi^p(T)$ denote the characters of the irreducible representation Γ^p and $\chi(T)$ denote the characters of the reducible representation Γ .

Proof. The theorem follows from evaluating the sum on the right-hand side of the equation above. From Theorem 18 it is known that for a reducible representation

the following equation holds,

$$\chi(T) = \sum_{q=1}^N n_q \chi^q(T), \quad (5.39)$$

where N denotes the number of inequivalent irreducible representations. Therefore, it follows by means of the orthogonality theorem for characters (Theorem 19) that

$$\sum_{T \in \mathcal{G}} [\chi^p(T)]^* \chi(T) = \sum_{q=1}^N n_q \underbrace{\sum_{T \in \mathcal{G}} [\chi^p(T)]^* \chi^q(T)}_{g \delta_{p,q}} = g \sum_{q=1}^N n_q \delta_{p,q} = g n_p. \quad (5.40)$$

□

Equation (5.38) is implemented within the command **GTlrep** in GTPack. As a consequence of Theorem 21 it will be shown that the dimensions of the irreducible representations are restricted by the group order.

Theorem 22 (Dimensions of irreducible representations). *Consider a group $\mathcal{G}$ with order g . Let l_p be the dimension of an irreducible representation Γ^p of $\mathcal{G}$ and N the number of inequivalent irreducible representations of $\mathcal{G}$, then the sum of the squares of the dimensions l_p is equal to the group order g ,*

$$\sum_{p=1}^N l_p^2 = g. \quad (5.41)$$

Proof. The theorem can be proven with the help of the regular representation Γ^{reg} (see Definition 27). In Example 24 the characters $\chi^{\text{reg}}(T)$ of the elements T were calculated and it was shown that

$$\chi^{\text{reg}}(T) = \begin{cases} 0 & T \neq E \\ g & T = E \end{cases}. \quad (5.42)$$

By applying Theorem 21 to calculate the number of times l_p an irreducible representation Γ^p occurs within Γ^{reg} , it is possible to verify that Γ^p appears exactly l_p times,

$$n_p = \frac{1}{g} \sum_{T \in \mathcal{G}} [\chi^p(T)]^* \chi^{\text{reg}}(T) = \frac{1}{g} [\chi^p(E)]^* \chi^{\text{reg}}(E) = \frac{1}{g} l_p g = l_p. \quad (5.43)$$

Finally, by referring to Theorem 18 and setting $T = E$ it is possible to prove the assumption,

$$g = \chi^{\text{reg}}(E) = \sum_{p=1}^N n_p \chi^p(E) = \sum_{p=1}^N l_p \cdot l_p = \sum_{p=1}^N l_p^2. \quad (5.44)$$

□

Example 27 (Decomposition of the regular representation.). Within the proof of Theorem 22 it was shown that each l_p -dimensional irreducible representation Γ^p occurs l_p times within the regular representation,

$$\Gamma^{\text{reg}} \simeq l_1 \Gamma^1 \oplus l_2 \Gamma^2 \oplus \dots \quad (5.45)$$

To calculate the number of times an irreducible representation appears within a reducible representation, the command **GTIrep** can be applied. An example for the point group C_{4v} is shown in Figure 5.8. The input of **GTIrep** is the character system of the reducible representation (i.e., the character of a certain element of each class – according to Theorem 17 every element in a certain class has the same character) as well as the character table of the point group. To calculate the character system of the regular representation **GTClasses** can be used to estimate the classes of C_{4v} . Afterwards, the character can be computed by taking the trace. To

Mathematica

GTIrep

At first, the point group C_{4v} and its regular representation is installed.

```
In[9]:= c4v = GTInstallGroup[C4v, GVerbose -> False];
reg = GTRegularRepresentation[c4v];
```

Using **GTClasses** for the regular representation of C_{4v} the character system is calculated by taking the trace of the first element of each class.

```
In[11]:= classes = GTClasses[reg];
charsystem = Table[Tr[classes[[i, 1]]], {i, 1, Length[classes]}]

Out[12]:= {8, 0, 0, 0, 0, 0}
```

For the command **GTIrep** the character table is needed, which is installed by means of **GTCharacterTable**.

```
In[13]:= charactertable = GTCharacterTable[c4v, GOpIrepNotation -> "Mulliken"];
```

	Ee	2 IC _{2x}	2 IC _{2a}	2 C _{4z} ¹	C _{2z}
A ₁	1	1	1	1	1
A ₂	1	-1	-1	1	1
B ₂	1	-1	1	-1	1
B ₁	1	1	-1	-1	1
E	2	0	0	0	-2

$C_1 = \{Ee\}$

$C_2 = \{IC_{2x}, IC_{2y}\}$

$C_3 = \{IC_{2a}, IC_{2b}\}$

$C_4 = \{C_{4z}^1, C_{4z}^3\}$

$C_5 = \{C_{2z}\}$

Using **GTIrep** it can be verified that each one-dimensional representation occurs once, but the two-dimensional representation E occurs twice.

```
In[14]:= GTIrep[charsystem, charactertable]
```

$A_1 \oplus A_2 \oplus B_2 \oplus B_1 \oplus 2 E$

```
Out[14]:= {1, 1, 1, 1, 2}
```

Figure 5.8 Decomposition of the regular representation of the point group C_{4v} using **GTIrep**.

estimate the character table **GTCharacterTable** is used and the MULLIKEN notation is chosen. C_{4v} has four 1-dimensional representations (A_1, A_2, B_1, B_2) as well as one 2-dimensional representation E . As expected, each irreducible representation occurs once except for E , which occurs twice within the regular representation,

$$\Gamma^{\text{reg}}(C_{4v}) \simeq A_1 \oplus A_2 \oplus B_1 \oplus B_2 \oplus 2E. \quad (5.46)$$

Task 18 (Decomposition into irreducible representations). Install the point group O and calculate its character table.

1. Verify Theorem 22.
2. Install the regular representation and decompose it into irreducible representations (follow Example 27).

5.4

Projection Operators and Basis Functions of Representations

Projection operators	
GTProjectionOperator	Applies the projection operator to a given function
GTCharProjectionOperator	Applies the character projection operator to a given function
GTWignerProjectionOperator	Applies the projection operator to spherical harmonics

For each group $\mathcal{G}$ of coordinate transformations and a representation Γ (which can be reducible in general) it is possible to define a set of basis functions.

Definition 31 (Basis functions). *For a given l -dimensional representation Γ of a group $\mathcal{G}$ a set of l functions $\phi_1, \dots, \phi_l$ is called a set of basis functions if the following relation holds for every coordinate transformation associated with $T \in \mathcal{G}$,*

$$\hat{P}(T)\phi_n(\mathbf{r}) = \sum_{m=1}^l \Gamma_{mn}(T)\phi_m(\mathbf{r}). \quad (5.47)$$

The definition of basis functions is based on the particular transformation behavior of a set of functions $\{\phi_1, \dots, \phi_l\}$ under coordinate transformations. However, basis functions for a representation Γ of a finite group $\mathcal{G}$ are not defined uniquely and an infinite amount of sets of functions can be found that satisfy equation (5.47).

In the following, all functions are elements of a HILBERT space. Because of the orthogonality of the representation matrices of irreducible representations, also the basis functions have to be orthogonal.

Theorem 23 (Orthogonality of basis functions of irreducible representations). *Let Γ^p and Γ^q be two irreducible representations of a group $\mathcal{G}$ with basis functions $\phi_1^p, \dots, \phi_{l_p}^p$ and $\phi_1^q, \dots, \phi_{l_q}^q$, respectively. For $p \neq q$ and $m \neq n$, the following orthogonality relation holds*

$$(\phi_m^p, \phi_n^q) = 0. \quad (5.48)$$

Proof. To prove equation (5.48) the inner product (ϕ_m^p, ϕ_n^q) within the HILBERT space¹²⁾ has to be evaluated. The inner product has to be invariant under coordinate transformations,

$$(\phi_m^p, \phi_n^q) = (\hat{P}(T) \phi_m^p, \hat{P}(T) \phi_n^q) \quad (5.50)$$

$$= \sum_{i=1}^{l_p} \sum_{j=1}^{l_q} \Gamma_{im}^p(T)^* \Gamma_{jn}^q(T) (\phi_i^p, \phi_j^q). \quad (5.51)$$

Summation over all possible transformations $T \in \mathcal{G}$ allows the application of the orthogonality theorem (Theorem 16),

$$g(\phi_m^p, \phi_n^q) = \sum_{i=1}^{l_p} \sum_{j=1}^{l_q} \sum_{T \in \mathcal{G}} \Gamma_{im}^p(T)^* \Gamma_{jn}^q(T) (\phi_i^p, \phi_j^q) \quad (5.52)$$

$$= \delta_{p,q} \delta_{m,n} \underbrace{\frac{g}{l_p} \sum_{i=1}^{l_p} (\phi_i^p, \phi_i^p)}_{= \text{const.}}. \quad (5.53)$$

□

In general, each function $\Phi(\mathbf{r})$ can be separated into a finite sum of basis functions,

$$\Phi(\mathbf{r}) = \sum_{p=1}^N \sum_{m=1}^{l_p} \phi_m^p(\mathbf{r}), \quad (5.54)$$

where N denotes the number of inequivalent irreducible representations. An expansion according to (5.54) can be found by applying projection operators $\hat{P}_{nn}^p$ that project out the part of a function transforming like the n th row of an irreducible representation Γ^p . In the following, the derivation of such operators will be discussed and without loss of generality it is assumed that the basis functions are normalized. For its construction, it is expected that for a given set of basis

12) For the space L^2 of square integrable functions the inner product is given by

$$(\phi_m^p, \phi_n^q) = \int d^3r \phi_m^p(\mathbf{r})^* \phi_n^q(\mathbf{r}). \quad (5.49)$$

functions $\phi_1^p, \dots, \phi_{l_p}^p$ of an irreducible representation Γ^p , the following relation has to be satisfied,

$$\hat{\mathcal{P}}_{nm}^p \phi_k^q(\mathbf{r}) = \delta_{p,q} \delta_{m,k} \phi_n^p(\mathbf{r}). \quad (5.55)$$

It follows that $\phi_n^p(\mathbf{r})$ is an eigenfunction of $\hat{\mathcal{P}}_{nn}^p$ with eigenvalue 1. Applying a diagonal element of the projection operator to an arbitrary function (cf. (5.54)), one obtains

$$\hat{\mathcal{P}}_{mm}^p \Phi(\mathbf{r}) = \sum_{q=1}^N \sum_{k=1}^{l_q} \hat{\mathcal{P}}_{mm}^p \phi_k^q(\mathbf{r}) = \phi_m^p(\mathbf{r}). \quad (5.56)$$

Let's furthermore consider that the general form of the projection operator $\hat{\mathcal{P}}_{mn}^p$ can be written as

$$\hat{\mathcal{P}}_{mn}^p = \sum_{T \in \mathcal{G}} B_{mn}^p(T) \hat{P}(T). \quad (5.57)$$

Without loss of generality it is assumed that the basis functions are normalized in the following, $(\phi_m^p, \phi_m^p) = 1$. It follows that the matrix elements of the projection operator are given by

$$(\phi_m^p, \hat{\mathcal{P}}_{mn}^p \phi_n^p) = (\phi_m^p, \phi_m^p) = 1 \quad (5.58)$$

$$= \sum_{T \in \mathcal{G}} B_{mn}^p(T) (\phi_m^p, \hat{P}(T) \phi_n^p) \quad (5.59)$$

$$= \sum_{T \in \mathcal{G}} B_{mn}^p(T) \Gamma_{mn}^p(T). \quad (5.60)$$

The last identity from (5.59) to (5.60) follows from (5.47), multiplying from the left-hand side with $\phi_m^p(\mathbf{r})^*$ and integrating over $\mathbf{r}$, which leads to the identity $(\phi_m^p, \hat{P}(T) \phi_n^p) = \Gamma_{mn}^p(T)$. With the help of the orthogonality theorem for irreducible representations (Theorem 16) and equation (5.23), the coefficients $B_{mn}^p(T)$ can be identified by $B_{mn}^p(T) = \frac{l_p}{g} \Gamma_{mn}^p(T)^*$. Hence, the projection operator can be written as

$$\hat{\mathcal{P}}_{mn}^p = \frac{l_p}{g} \sum_{T \in \mathcal{G}} \Gamma_{mn}^p(T)^* \hat{P}(T). \quad (5.61)$$

Next to the projection operator (5.61) it is possible to define the character projection operator $\hat{\mathcal{P}}^p$ by summation over the operators $\hat{\mathcal{P}}_{mm}^p$,

$$\hat{\mathcal{P}}^p = \sum_{m=1}^{l_p} \hat{\mathcal{P}}_{mm}^p = \frac{l_p}{g} \sum_{T \in \mathcal{G}} \chi^p(T)^* \hat{P}(T). \quad (5.62)$$

The application of the character projection operator gives a linear combination of the basis functions $\phi_1^p, \dots, \phi_{l_p}^p$. However, as any linear combination of basis

functions will give again a basis function, the result is another basis function $\tilde{\phi}_1^p$. Hence, the character projection operator can be used to determine a first basis function if only the character system and not the representation matrices are known.

Example 28 (The projection operator within GTPack). As an example the three projection operators $\hat{P}_{11}$, $\hat{P}_{22}$, and $\hat{P}_{33}$ of the irreducible representation T_2 (see character table in Figure 5.9) of the point group O will be applied to the function

$$f(x, y, z) = x + y + z + x^2. \quad (5.63)$$

As shown in Figure 5.9 the projection operator $\hat{P}_{1i}$ can be applied by using the command **GTProjectionOperator**. For this, the matrices of the irreducible representation T_2 need to be generated which can be done using **GTGetIrep**. According to Figure 5.9, three basis functions can be found, which are given by,

$$\hat{P}_{11}f(x, y, z) = y, \quad (5.64)$$

$$\hat{P}_{22}f(x, y, z) = z, \quad (5.65)$$

$$\hat{P}_{33}f(x, y, z) = x. \quad (5.66)$$

Analogously, the character projection operator can be applied using **GTCharProjectionOperator**. The result is given by a linear combination of (5.64)–(5.66),

$$\hat{P}f(x, y, z) = x + y + z. \quad (5.67)$$

Example 29 (Calculating representation matrices from basis functions). The definition of basis functions $\phi_1^p, \dots, \phi_{l_p}^p$ of an irreducible representation Γ^p (Definition 31) is given by the transformation behavior of each function ϕ_n^p under coordinate transformations,

$$\hat{P}(T)\phi_n^p(\mathbf{r}) = \sum_{m=1}^{l_p} \Gamma_{nm}^p(T) \phi_m^p(\mathbf{r}). \quad (5.68)$$

Equation (5.68) can be used to calculate the matrix elements $\Gamma_{nm}^p(T)$ of a representation matrix $\underline{\Gamma}^p(T)$ as soon as a set of basis functions is known. Such a set can be obtained by starting with an orthonormal basis and applying the character projection operator. A good choice for such a basis are the tesseral harmonics or real spherical harmonics S_l^m (see Appendix A.2.2). These functions can be evaluated in Cartesian form using the command **GTCartesianTesseralHarmonicY** (see Figure 5.10). For $l = 2$ and avoiding the spherically symmetric factor $(x^2 + y^2 + z^2)$

Mathematica**GTProjectionOperator, GTCharProjectionOperator**

At first the group O is installed and the character table is calculated.

```
In[9]:= o = GTInstallGroup[O]
```

The standard representation has changed to $O(3)$

```
Out[9]:= {Ee, C2z, C2f, C2e, C2y, C2b, C2d, C2c, C2a, C2x, C3b,
          C3y, C3y^-1, C3a^-1, C3b^-1, C3b, C3a, C3b, C4z, C4y, C4y^-1, C4z, C4x^-1, C4x}
```

```
In[10]:= charactertable =
```

```
{classes, chars, names} = GTCharacterTable[o, GOIrepNotation -> "Mulliken"];
```

	Ee	3 C _{2z}	6 C _{2f}	6 C _{4z} ⁻¹	8 C _{3b}
A ₁	1	1	1	1	1
A ₂	1	1	-1	-1	1
E	2	2	0	0	-1
T ₂	3	-1	-1	1	0
T ₁	3	-1	1	-1	0

```
C1 = {Ee}
```

```
C2 = {C2z, C2y, C2x}
```

```
C3 = {C2f, C2e, C2b, C2d, C2c, C2a}
```

```
C4 = {C4z, C4y, C4y^-1, C4z, C4x, C4x^-1}
```

```
C5 = {C3b, C3y, C3y^-1, C3a^-1, C3b^-1, C3b, C3a, C3b}
```

Matrices of the irreducible representation T_2 are computed using GTGetIrep.

```
In[11]:= Ir2 = GTGetIrep[o, 4, charactertable, GOMethod -> "Cornwell"];
```

The projection operator is applied to the function $f(x, y, z) = x + y + z + x^2$.

```
In[12]:= f[x_, y_, z_] = x + y + z + x^2;
```

```
In[13]:= GTProjectionOperator[o, Ir2, 1, 1, f, {x, y, z}]
```

```
Out[13]:= y
```

```
In[14]:= GTProjectionOperator[o, Ir2, 2, 2, f, {x, y, z}]
```

```
Out[14]:= z
```

```
In[15]:= GTProjectionOperator[o, Ir2, 3, 3, f, {x, y, z}]
```

```
Out[15]:= x
```

Using GTCharProjectionOperator, the character projection operator is applied.

```
In[16]:= GTCharProjectionOperator[classes, chars[[4]], f, {x, y, z}]
```

```
Out[16]:= x + y + z
```

Figure 5.9 Application of the projection operator and the character projection operator using GTProjectionOperator and GTCharProjectionOperator.

Mathematica**GTCartesianTesseralHarmonics, GTCharProjectionOperator**

The Cartesian tesseral harmonics for $l = 2$

In[17]:= **fm2**[**x_**, **y_**, **z_**] = **GTCartesianTesseralHarmonicY**[2, -2, **x**, **y**, **z**] * (**x**² + **y**² + **z**²)

Out[17]= $\frac{1}{2} \sqrt{\frac{15}{\pi}} x y$

In[18]:= **fm1**[**x_**, **y_**, **z_**] = **GTCartesianTesseralHarmonicY**[2, -1, **x**, **y**, **z**] * (**x**² + **y**² + **z**²)

Out[18]= $\frac{1}{2} \sqrt{\frac{15}{\pi}} y z$

In[19]:= **f0**[**x_**, **y_**, **z_**] = **GTCartesianTesseralHarmonicY**[2, 0, **x**, **y**, **z**] * (**x**² + **y**² + **z**²)

Out[19]= $-\frac{1}{4} \sqrt{\frac{5}{\pi}} (x^2 + y^2 - 2 z^2)$

In[20]:= **fp1**[**x_**, **y_**, **z_**] = **GTCartesianTesseralHarmonicY**[2, 1, **x**, **y**, **z**] * (**x**² + **y**² + **z**²)

Out[20]= $\frac{1}{2} \sqrt{\frac{15}{\pi}} x z$

In[21]:= **fp2**[**x_**, **y_**, **z_**] = **GTCartesianTesseralHarmonicY**[2, 2, **x**, **y**, **z**] * (**x**² + **y**² + **z**²)

Out[21]= $\frac{1}{4} \sqrt{\frac{15}{\pi}} (x^2 - y^2)$

Application of the character projection operator.

In[22]:= **GTCharProjectionOperator**[**classes**, **chars**[**[5]**], **fm2**, {**x**, **y**, **z**}]
GTCharProjectionOperator[**classes**, **chars**[**[5]**], **fm1**, {**x**, **y**, **z**}]
GTCharProjectionOperator[**classes**, **chars**[**[5]**], **f0**, {**x**, **y**, **z**}]
GTCharProjectionOperator[**classes**, **chars**[**[5]**], **fp1**, {**x**, **y**, **z**}]
GTCharProjectionOperator[**classes**, **chars**[**[5]**], **fp2**, {**x**, **y**, **z**}]

Out[22]= $\frac{1}{2} \sqrt{\frac{15}{\pi}} x y$

Out[23]= $\frac{1}{2} \sqrt{\frac{15}{\pi}} y z$

Out[24]= 0

Out[25]= $\frac{1}{2} \sqrt{\frac{15}{\pi}} x z$

Out[26]= 0

Figure 5.10 Application of the character projection operator of the irreducible representation T_1 of the point group O to the Cartesian tesseral harmonics with $l = 2$.

as well as the normalization coefficients these functions are given by

$$S_{-2}^2 \simeq xy, \quad (5.69)$$

$$S_{-1}^2 \simeq yz, \quad (5.70)$$

$$S_0^2 \simeq x^2 + y^2 - 2z^2, \quad (5.71)$$

$$S_1^2 \simeq xz, \quad (5.72)$$

$$S_2^2 \simeq x^2 - y^2. \quad (5.73)$$

Using the point group O as in the previous example (Example 28) but the irreducible representation T_1 , the application of the character projection operator to the Cartesian tesseral harmonics gives

$$\hat{P}S_{-2}^2 = S_{-2}^2, \quad (5.74)$$

$$\hat{P}S_{-1}^2 = S_{-1}^2, \quad (5.75)$$

$$\hat{P}S_0^2 = 0, \quad (5.76)$$

$$\hat{P}S_1^2 = S_1^2, \quad (5.77)$$

$$\hat{P}S_2^2 = 0. \quad (5.78)$$

Hence, S_{-2}^2 , S_{-1}^2 , and S_1^2 can be seen as basis functions of the irreducible representation T_1 . A coordinate transformation with respect to C_{4z} acts as

$$x \rightarrow y, \quad y \rightarrow -x, \quad z \rightarrow z. \quad (5.79)$$

Coordinate transformations can be performed automatically using **GTTransformationOperator**. An example can be found in Figure 5.11. For C_{4z} , it follows

$$\hat{P}(C_{4z}) S_{-2}^2 = -S_{-2}^2 = -1 \cdot S_{-2}^2 + 0 \cdot S_{-1}^2 + 0 \cdot S_1^2, \quad (5.80)$$

$$\hat{P}(C_{4z}) S_{-1}^2 = -S_1^2 = 0 \cdot S_{-2}^2 + 0 \cdot S_{-1}^2 - 1 \cdot S_1^2, \quad (5.81)$$

$$\hat{P}(C_{4z}) S_1^2 = S_{-1}^2 = 0 \cdot S_{-2}^2 + 1 \cdot S_{-1}^2 + 0 \cdot S_1^2. \quad (5.82)$$

Hence, the representation matrix can be written as

$$\underline{\Gamma}^{T_1}(C_{4z}) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}. \quad (5.83)$$

This algorithm for calculating the representation matrices can be used by means of **GTGetIrep** and specifying the option **Method**→"Cornwell"¹³.

13) According to CORNWELL [36].

Mathematica
GTTransformationOperator

```
In[27]:= GTTransformationOperator[C4z, fm2, {x, y, z}]
```

$$\text{Out[27]} = -\frac{1}{2} \sqrt{\frac{15}{\pi}} \, x \, y$$

```
In[28]:= GTTransformationOperator[C4z, fm1, {x, y, z}]
```

$$\text{Out[28]} = -\frac{1}{2} \sqrt{\frac{15}{\pi}} \, x \, z$$

```
In[29]:= GTTransformationOperator[C4z, fp1, {x, y, z}]
```

$$\text{Out[29]} = \frac{1}{2} \sqrt{\frac{15}{\pi}} \, y \, z$$

```
In[30]:= GTTransformationOperator[C4z, f, {x, y, z}]
```

$$\text{Out[30]} = -x + y + y^2 + z$$

Figure 5.11 Application of the transformation operator of the element C_{4z} to the basis functions of the irreducible representation T_2 of the point group O (Functions are defined in Figure 5.10).

Task 19 (Character projection operator). Apply the character projection operator (**GTCharProjectionOperator**) associated with each irreducible representation of the point group C_{3v} to the function

$$f(x, y, z) = (x + y + z)^2. \tag{5.84}$$

5.5
Direct Product Representations

Direct product representations	
GTDirectProductRep	Calculates the direct product of two matrix representations
GTDirectProductChars	Calculates the character system of the direct product representation of two matrix representations
GTClebschGordanCoefficients	Calculates the CLEBSCH–GORDAN coefficients
GTClebschGordanTable	Illustrates calculated CLEBSCH–GORDAN coefficients

The aim of this section is to define and investigate matrix representations of direct product groups which were introduced in Section 3.4, Definition 17. The direct product or **KRONECKER** product of two matrices is given by

$$\underline{\underline{A}} \otimes \underline{\underline{B}} = \begin{pmatrix} A_{11}\underline{\underline{B}} & \cdots & A_{1n}\underline{\underline{B}} \\ \vdots & \ddots & \vdots \\ A_{n1}\underline{\underline{B}} & \cdots & A_{nn}\underline{\underline{B}} \end{pmatrix}. \quad (5.85)$$

Using the index notation, equation (5.85) can be expressed as $(\underline{\underline{A}} \otimes \underline{\underline{B}})_{js,kt} = A_{jk}B_{st}$. If two representations of two finite groups $\mathcal{G}_1$ and $\mathcal{G}_2$ are known, the concept of the direct product of matrices can be applied to construct a matrix representation of a direct product group $\mathcal{G}_1 \times \mathcal{G}_2$.

Theorem 24 (Direct product representation). *Let Γ^1 and Γ^2 be two l_1 - and l_2 -dimensional representations of the groups $\mathcal{G}_1$ and $\mathcal{G}_2$ with elements $T \in \mathcal{G}_1$ and $S \in \mathcal{G}_2$. Then, the matrices $\underline{\underline{\Gamma}}(T, S) = \underline{\underline{\Gamma}}^1(T) \otimes \underline{\underline{\Gamma}}^2(S)$ form a matrix representation of the direct product group $\mathcal{G}_1 \times \mathcal{G}_2$. The so-formed matrix representation is called the direct product representation of the direct product group $\mathcal{G}_1 \times \mathcal{G}_2$.*

Proof. It has to be shown that $\underline{\underline{\Gamma}}(TT', SS') = \underline{\underline{\Gamma}}(T, S) \cdot \underline{\underline{\Gamma}}(T', S')$. The definition of the direct product of matrices gives $\underline{\underline{\Gamma}}(T, S)_{js,kt} = \Gamma^1(T)_{jk}\Gamma^2(S)_{st}$. Hence, the matrix product $\underline{\underline{\Gamma}}(T, S) \cdot \underline{\underline{\Gamma}}(T', S')$ can be calculated explicitly,

$$\begin{aligned} \sum_{k=1}^{l_1} \sum_{t=1}^{l_2} \underline{\underline{\Gamma}}(T, S)_{js,kt} \underline{\underline{\Gamma}}(T', S')_{kt,lu} &= \sum_{k=1}^{l_1} \sum_{t=1}^{l_2} \Gamma^1(T)_{jk} \Gamma^2(S)_{st} \Gamma^1(T')_{kl} \Gamma^2(S')_{tu} \\ &= \sum_{k=1}^{l_1} \Gamma^1(T)_{jk} \Gamma^1(T')_{kl} \sum_{t=1}^{l_2} \Gamma^2(S)_{st} \Gamma^2(S')_{tu} \\ &= \Gamma^1(TT')_{jl} \Gamma^2(SS')_{su} \\ &= \underline{\underline{\Gamma}}(TT', SS')_{js,lu}. \end{aligned} \quad (5.86)$$

□

According to equation (5.85), the dimension of the direct product representation $\Gamma^1 \otimes \Gamma^2$ is given by the product of the dimensions of Γ^1 and Γ^2 . To install direct product representations from two given matrix representations within **GTPack** the command **GTDirectProductRep** can be used, as will be explained in Example 30. It can be shown that if $\mathcal{G}_1 \times \mathcal{G}_2$ is a finite group and if Γ^1 and Γ^2 are irreducible representations of $\mathcal{G}_1$ and $\mathcal{G}_2$, respectively, then the direct product representation $\Gamma^1 \otimes \Gamma^2$ is an irreducible representation of the direct product group $\mathcal{G}_1 \times \mathcal{G}_2$ [36].

A special case occurs if $\mathcal{G}_1$ and $\mathcal{G}_2$ are isomorphic to the same group $\mathcal{G}$. Then, the direct product group $\mathcal{G} \times \mathcal{G}$ has a diagonal subgroup $\mathcal{G}' \subset \mathcal{G} \times \mathcal{G}$ with elements $(T, T) \in \mathcal{G}'$, which is again isomorphic to $\mathcal{G}$. However, the direct product representation of two irreducible representations Γ^p and Γ^q of $\mathcal{G}$ does not form an irreducible representation of the diagonal subgroup $\mathcal{G}' \cong \mathcal{G}$. The following results

reflect properties of the diagonal subgroup of the direct product representation $\mathcal{G} \times \mathcal{G}$.

Theorem 25 (Characters of a direct product representation). *For two given irreducible representations Γ^p and Γ^q of a group $\mathcal{G}$ with elements $T \in \mathcal{G}$ and characters $\chi^p(T)$ and $\chi^q(T)$, respectively, the characters of the direct product representation $\Gamma^{p \otimes q}$ of the diagonal subgroup of $\mathcal{G} \times \mathcal{G}$ are given by*

$$\chi^{p \otimes q}(T) = \chi^p(T) \chi^q(T). \quad (5.87)$$

Proof. Equation (5.87) can be verified by calculating the trace of the representation matrix $\underline{\Gamma}^{p \otimes q}(T) = \underline{\Gamma}^p(T) \otimes \underline{\Gamma}^q(T)$,

$$\begin{aligned} \chi^{p \otimes q}(T) &= \sum_{kt} \Gamma(T)_{kt, kt}^{p \otimes q} \\ &= \sum_{kt} \Gamma^p(T)_{kk} \Gamma^q(T)_{tt} \\ &= \left[\sum_k \Gamma^p(T)_{kk} \right] \left[\sum_t \Gamma^q(T)_{tt} \right] \\ &= \chi^p(T) \chi^q(T). \end{aligned} \quad (5.88)$$

□

In general, the direct product representation $\Gamma^{p \otimes q}$ of the diagonal subgroup is reducible and it is of practical importance to verify which irreducible representations occur. With the help of Theorem 25 it is easy to calculate the character system of $\Gamma^{p \otimes q}$ and afterwards Theorem 21 can be applied (see Example 31).

More generally, assuming that the group $\mathcal{G}$ has h inequivalent irreducible representations, then, $\Gamma^{p \otimes q}$ can be expressed by a CLEBSCH–GORDAN sum of the form

$$\Gamma^p \otimes \Gamma^q \simeq n_1 \Gamma^1 \oplus n_2 \Gamma^2 \oplus \cdots \oplus n_h \Gamma^h, \quad (5.89)$$

where n_i denotes the number of times an irreducible representation Γ^i occurs (it is possible that $n_i = 0$). Suppose, the basis functions $\phi_1^p, \dots, \phi_{l_p}^p$ and $\phi_1^q, \dots, \phi_{l_q}^q$ of the irreducible representations Γ^p and Γ^q are known (l_p is the dimension of Γ^p and l_q the dimension of Γ^q), then it is possible to construct $l_p \times l_q$ products $\phi_j^p \phi_k^q$, which form the basis of a $l_p \times l_q$ -dimensional vector space $\mathcal{V}$,

$$B_1 = \left\{ \phi_j^p \phi_k^q, j = 1, \dots, l_p; k = 1, \dots, l_q \right\} \quad (5.90)$$

From equation (5.89) it follows that $\mathcal{V}$ can be separated into several subspaces with the basis functions $\psi_i^{r, \alpha}(\mathbf{r})$, where r is related to an irreducible representation Γ^r , $i = 1, \dots, l_r$ denotes the l_r -dimensional basis of the subspace, and $\alpha = 1, \dots, n_r$ counts the number of times Γ^r occurs in (5.89). The elements $\psi_i^{r, \alpha}$ form a second

basis of $\mathcal{V}$, denoted by $\mathcal{B}_2$. However, since $\mathcal{B}_1$ is a basis of $\mathcal{V}$, the functions $\psi_i^{r,\alpha}$ can be expressed in terms of $\phi_j^p \phi_k^q$ by

$$\psi_i^{r,\alpha}(\mathbf{r}) = \sum_{j=1}^{l_p} \sum_{k=1}^{l_q} \left(\begin{matrix} p & q \\ j & k \end{matrix} \middle| \begin{matrix} r, & \alpha \\ i \end{matrix} \right) \phi_j^p(\mathbf{r}) \phi_k^q(\mathbf{r}). \quad (5.91)$$

The coefficients $\left(\begin{matrix} p & q \\ j & k \end{matrix} \middle| \begin{matrix} r, & \alpha \\ i \end{matrix} \right)$ are called CLEBSCH–GORDAN coefficients and are formally defined by

$$\left(\begin{matrix} p & q \\ j & k \end{matrix} \middle| \begin{matrix} r, & \alpha \\ i \end{matrix} \right) = \int d^3\mathbf{r} \phi_j^p(\mathbf{r})^* \phi_k^q(\mathbf{r})^* \psi_i^{r,\alpha}(\mathbf{r}). \quad (5.92)$$

Vice versa, $\phi_j^p \phi_k^q$ can be calculated using functions $\psi_i^{r,\alpha}$ of the basis $\mathcal{B}_2$ by

$$\phi_j^p(\mathbf{r}) \phi_k^q(\mathbf{r}) = \sum_{r=1}^h \sum_{i=1}^{l_r} \sum_{\alpha=1}^{n_r} \left(\begin{matrix} r, & \alpha \\ i \end{matrix} \middle| \begin{matrix} p & q \\ j & k \end{matrix} \right) \psi_i^{r,\alpha}(\mathbf{r}). \quad (5.93)$$

Example 30 (Direct product representations in GTPack). Subsequently, the group C_{3v} is chosen and the direct product representation $E \otimes E$ of the 2-dimensional irreducible representation E with itself is calculated. The matrices of E can be obtained by applying **GTGetIrep**. As shown in Figure 5.12, the direct product representation is calculated by means of **GTDirectProductRep**. Alternatively to **GTDirectProductRep**, the operator $\otimes$ can be used within the *Mathematica* notebook¹⁴. Since E is a 2-dimensional representation, the direct product $\Gamma^{E \otimes E}$ is a 4-dimensional representation. **GTDirectProductRep** automatically calculates the direct product representation for the diagonal subgroup. If the representation of the whole direct product group is needed, the option **GODiagonal**→False can be specified.

Example 31 (Characters of a direct product representation). In connection to Example 30, the characters of the direct product representation $\Gamma^{E \otimes E}$ of the point group C_{3v} are calculated by using **GTDirectProductChars**. The character system of the irreducible representation E , which is needed for the computation, is obtained by means of **GTCharacterTable** (see Figure 5.13). Since $\Gamma^{E \otimes E}$ is a 4-dimensional representation and the highest possible dimension of an irreducible representation of C_{3v} is equal to 2, it can be concluded that $\Gamma^{E \otimes E}$ has to be reducible. Using **GTIrep** it can be verified that $\Gamma^{E \otimes E}$ can be decomposed into A_1 , A_2 , and E ,

$$E \simeq A_1 \oplus A_2 \oplus E. \quad (5.94)$$

14) Within *Mathematica* the operator $\otimes$ can be generated by `\[CircleTimes]` or typing the sequence ESC c* ESC.

Mathematica

GTDirectProductRep

```
In[9]:= c3v = GTInstallGroup[C3v]
```

The standard representation has changed to $O(3)$

$$\text{Out}[9]= \{ \text{Ee}, \text{C}_{3z}, \text{C}_{3z}^{-1}, \text{IC}_{2D}, \text{IC}_{2C}, \text{IC}_{2Y} \}$$

The representation matrices of the two-dimensional irreducible representation E are given by

```
In[10]:= IrE = GTGetIrep[c3v, 3];
```

```
In[11]:= Map[MatrixForm, IrE]
```

$$\text{Out}(\{1\}) = \left\{ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} -\frac{1}{2} \mathbf{i} & (-\mathbf{i} + \sqrt{3}) \\ 0 & \frac{1}{2} \mathbf{i} \end{pmatrix}, \begin{pmatrix} \frac{1}{2} \mathbf{i} & (\mathbf{i} + \sqrt{3}) \\ 0 & -\frac{1}{2} \mathbf{i} \end{pmatrix}, \right. \\ \left. \begin{pmatrix} 0 & \frac{1}{2} \mathbf{i} \end{pmatrix}, \begin{pmatrix} 0 & -\frac{1}{2} \mathbf{i} \end{pmatrix}, \begin{pmatrix} -\frac{1}{2} \mathbf{i} & (-\mathbf{i} + \sqrt{3}) \\ 0 & 0 \end{pmatrix}, \begin{pmatrix} \frac{1}{2} \mathbf{i} & (\mathbf{i} + \sqrt{3}) \\ 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \right\}$$

The direct product representation $E \otimes E$ is calculated using `GTDirectProductRep`

```
In[12]:= dp = GTDirectProductRep[IrE, IrE];
```

```
In[13]:= Map[MatrixForm, dp] // FullSimplify
```

$$\text{Out}[13] = \left\{ \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} \frac{1}{2} i (i + \sqrt{3}) & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -(-1)^{1/3} \end{pmatrix}, \begin{pmatrix} -(-1)^{1/3} & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & \frac{1}{2} i (i + \sqrt{3}) \end{pmatrix}, \right.$$

$$\left. \begin{pmatrix} 0 & 0 & 0 & -(-1)^{1/3} \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ \frac{1}{2} i (i + \sqrt{3}) & 0 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 0 & \frac{1}{2} i (i + \sqrt{3}) \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -(-1)^{1/3} & 0 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \right\}$$

Alternatively, the symbolic form of `GTDirectProductRep` can be used

```
In[14]:= MatrixForm /@ FullSimplify@ (IrE⊗IrE)
```

$$\text{Out}[14] = \left\{ \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} \frac{1}{2} i (i + \sqrt{3}) & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -(-1)^{1/3} \end{pmatrix}, \begin{pmatrix} -(-1)^{1/3} & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & \frac{1}{2} i (i + \sqrt{3}) \end{pmatrix}, \right.$$

$$\left. \begin{pmatrix} 0 & 0 & 0 & -(-1)^{1/3} \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ \frac{1}{2} i (i + \sqrt{3}) & 0 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 0 & \frac{1}{2} i (i + \sqrt{3}) \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 \\ -(-1)^{1/3} & 0 & 0 & 0 \end{pmatrix}, \left. \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \right\}$$

Figure 5.12 Calculation of the direct product representation $E \otimes E$ for the group C_{3v} using `GTDirectProductRep`.

Mathematica**GTDirectProductChars**

The character table of C_{3v} .

```
In[9]:= c3v = GTInstallGroup[C3v, GVerbose -> False];
characterTable = GTCharacterTable[c3v, GOIrepNotation -> "Mulliken"]
```

	Ee	2 C_{3z}^{-1}	3 IC_{2D}
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

$C_1 = \{Ee\}$

$C_2 = \{C_{3z}^{-1}, C_{3z}\}$

$C_3 = \{IC_{2D}, IC_{2C}, IC_{2y}\}$

```
Out[10]= {{ {Ee}, {C_{3z}^{-1}, C_{3z}}, {IC_{2D}, IC_{2C}, IC_{2y}} }, {{1, 1, 1}, {1, 1, -1}, {2, -1, 0}}, {A_1, A_2, E} }
```

The characters of the irreducible representation E are given in the third row of the character table.

```
In[11]:= χE = characterTable[[2, 3]]
```

```
Out[11]= {2, -1, 0}
```

The character system of $E \otimes E$ is calculated using GTDirectProductChars.

```
In[12]:= χ = GTDirectProductChars[χE, χE]
```

```
Out[12]= {4, 1, 0}
```

Using GTIrep, it can be seen that $E \otimes E$ is reducible.

```
In[13]:= GTIrep[χ, characterTable, GOFast -> True]
```

$A_1 \oplus A_2 \oplus E$

```
Out[13]= {1, 1, 1}
```

Figure 5.13 Calculation of the character system of the direct product representation $\Gamma^{E \otimes E}$ of the point group C_{3v} .

Example 32 (CLEBSCH–GORDAN coefficients). In the previous example (Example 31), it was shown that the direct product representation $E \otimes E$ of the point group C_{3v} is reducible. Within the expansion as a CLEBSCH–GORDAN sum (5.94) each irreducible representation occurs once. From the representation matrices of each irreducible representation it is possible to evaluate the CLEBSCH–GORDAN coefficients with the help of the command **GTClebschGordanCoefficients**.¹⁵ The application of **GTClebschGordanCoefficients** is shown in Figure 5.14. To nicely represent CLEBSCH–GORDAN coefficients within a *Mathematica* notebook, **GTClebschGordanTable** can be used. The application of **GTClebschGordanCoefficients** and **GTClebschGordanTable** is illustrated in Figure 5.14. Suppose that $\phi_j^{E,1}$ ($j = 1, 2$) and $\phi_k^{E,2}$ ($k = 1, 2$) are two linear independent sets of basis functions of the irreducible representation E . With the help of the CLEBSCH–GORDAN coefficients the basis functions ψ_i^p ($p = A_1, A_2, E, i = 1, \dots, l_p$) of the direct product

15) For the calculation of CLEBSCH–GORDAN coefficients the algorithm of VAN DEN BROEK and CORNWELL [95] is used.

Mathematica**GTClebschGordanCoefficients, GTClebschGordanTable**

To calculate the Clebsch–Gordan coefficients for $E \otimes E \simeq A_1 \oplus A_2 \oplus E$, the representation matrices of A_1 , A_2 and E are needed.

```
In[9]:= ΓA1 = GTGetIrep[c3v, 1];
ΓA2 = GTGetIrep[c3v, 2];
ΓE = GTGetIrep[c3v, 3];
```

The Clebsch–Gordan coefficients $\begin{pmatrix} E & E & | & A_1 & 1 \\ j & k & | & 1 & 1 \end{pmatrix}$, $\begin{pmatrix} E & E & | & A_2 & 1 \\ j & k & | & 1 & 1 \end{pmatrix}$ and $\begin{pmatrix} E & E & | & E & 1 \\ j & k & | & i & 1 \end{pmatrix}$ are calculated using GTClebschGordanCoefficients.

```
In[12]:= cg1 = GTClebschGordanCoefficients[ΓE, ΓE, ΓA1]
```

```
Out[12]:= {{ {0,  $\frac{1}{\sqrt{2}}$ ,  $\frac{1}{\sqrt{2}}$ , 0} } }
```

```
In[13]:= cg2 = GTClebschGordanCoefficients[ΓE, ΓE, ΓA2]
```

```
Out[13]:= {{ {0,  $-\frac{1}{\sqrt{2}}$ ,  $\frac{1}{\sqrt{2}}$ , 0} } }
```

```
In[14]:= cg3 = GTClebschGordanCoefficients[ΓE, ΓE, ΓE]
```

```
Out[14]:= {{ {0, 0, 0, -1}, {-1, 0, 0, 0} } }
```

A table containing the Clebsch–Gordan coefficients can be printed using GTClebschGordanTable.

```
In[15]:= GTClebschGordanTable[ΓE, ΓE, {cg1, cg2, cg3}, {"A1", "A2", "E"}]
```

		A1	A2	E	
		1	1	1	
j	k	1	1	1	2
1	1	0	0	0	-1
1	2	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	0	0
2	1	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0	0
2	2	0	0	-1	0

Figure 5.14 Evaluation of CLEBSCH–GORDAN coefficients for the direct product representation $E \otimes E$ of the point group C_{3v} .

representation $E \otimes E$ can be estimated as follows,

$$\psi_1^{A_1,1} = \frac{1}{\sqrt{2}} (\phi_2^{E,1} \phi_1^{E,2} + \phi_1^{E,1} \phi_2^{E,2}) , \quad (5.95)$$

$$\psi_1^{A_2,1} = \frac{1}{\sqrt{2}} (\phi_2^{E,1} \phi_1^{E,2} - \phi_1^{E,1} \phi_2^{E,2}) , \quad (5.96)$$

$$\psi_1^{E,1} = -\phi_2^{E,1} \phi_2^{E,2} , \quad (5.97)$$

$$\psi_2^{E,1} = -\phi_1^{E,1} \phi_1^{E,2} . \quad (5.98)$$

Example 33 (Block diagonalization of direct product representations). Consider a group $\mathcal{G}$ and the direct product representation

$$\Gamma^p \otimes \Gamma^q \simeq n_1 \Gamma^1 \oplus \cdots \oplus n_N \Gamma^N. \quad (5.99)$$

Among others it is possible to think of two different sets of representation matrices for $\Gamma^p \otimes \Gamma^q$. One set can be found by constructing basis functions $\mathcal{B}_1$, according to equation (5.90), where $\phi_i(\mathbf{r}) = \phi_m^p(\mathbf{r})\phi_s^q(\mathbf{r})$. The index $i = 1, \dots, l_p l_q$ can be associated with the combined index (m, s) with $m = 1, \dots, l_p$ as well as $s = 1, \dots, l_q$ and a matrix representation can be constructed as follows,

$$\Gamma_{ij}^{p \otimes q}(T) = \left(\phi_i, \hat{P}(T) \phi_j \right) = \left(\phi_s^q \phi_m^p, \hat{P}(T) \phi_n^p \phi_t^q \right) = \Gamma_{ms, nt}^{p \otimes q}(T). \quad (5.100)$$

A second set can be constructed from the basis functions $\mathcal{B}_2$, choosing functions $\psi_i = \psi_c^{r, \alpha}$, where $i = 1, \dots, l_p l_q$ is associated with the combined index (r, α, c) . Here, r denotes an irreducible representation of the right-hand side of (5.99), $\alpha = 1, \dots, n_r$ and $c = 1, \dots, l_r$,

$$\tilde{\Gamma}_{ij}^{p \otimes q}(T) = \left(\psi_i, \hat{P}(T) \psi_j \right) = \delta_{r, r'} \left(\psi_c^{r, \alpha}, \hat{P}(T) \psi_d^{r', \alpha'} \right) = \tilde{\Gamma}_{rac, r' \alpha' d}^{p \otimes q}(T). \quad (5.101)$$

The delta function above can be verified from the transformation behavior of basis functions (5.47) and the orthogonality relation (5.48). Hence, $\tilde{\Gamma}^{p \otimes q}(T)$ is block diagonal with respect to the occurring irreducible representations. Of course it is possible to transform the basis $\mathcal{B}_1$ into the basis $\mathcal{B}_2$,

$$\psi_i(\mathbf{r}) = \sum_j U_{ij} \phi_j(\mathbf{r}). \quad (5.102)$$

According to (5.91) the entries of the transformation matrix $\underline{U}$ are the CLEBSCH–GORDAN coefficients,

$$U_{ij} = U_{rac, ms} = \left(\begin{matrix} p & q \\ m & s \end{matrix} \middle| \begin{matrix} r & \alpha \\ c \end{matrix} \right). \quad (5.103)$$

For C_{3v} and the direct product $E \otimes E$ it was shown in the previous examples that

$$E \otimes E \simeq A_1 \oplus A_2 \oplus E. \quad (5.104)$$

The calculation of the CLEBSCH–GORDAN coefficients was discussed in Example 32. Figure 5.15 illustrates how to block diagonalize $E \otimes E$ using GTPack.

Task 20 (CLEBSCH–GORDAN coefficients). Install the point group T_d .

1. Install the character table and use the MULLIKEN notation (**GTCharacterTable**).
2. Calculate the character system of the direct product representation $T_2 \otimes T_2$ (**GTDirectProductChars**).
3. Decompose the direct product representation into irreducible representations of T_d (**GTlrep**).
4. Calculate the related CLEBSCH–GORDAN coefficients (**GTclebschGordanCoefficients**) and illustrate them using **GTclebschGordanTable**.

Mathematica**GTDirectProductRep, GTClebschGordanCoefficients**

Calculation of the direct product representation $E \otimes E$.

In[16]:= **dp = TE ⊗ TE;**

In[17]:= **Map[MatrixForm, dp] // FullSimplify**

$$\text{Out[17]} = \left\{ \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} \frac{1}{2}i(i+\sqrt{3}) & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -(-1)^{1/3} \end{pmatrix}, \begin{pmatrix} -(-1)^{1/3} & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & \frac{1}{2}i(i+\sqrt{3}) \end{pmatrix}, \right.$$

$$\left. \begin{pmatrix} 0 & 0 & 0 & -(-1)^{1/3} \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ \frac{1}{2}i(i+\sqrt{3}) & 0 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 0 & \frac{1}{2}i(i+\sqrt{3}) \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -(-1)^{1/3} & 0 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \right\}$$

Estimate the transformation matrix from the Clebsch–Gordan–Coefficients.

In[18]:= **U = Flatten[{cg1, cg2, cg3}, 2];**

MatrixForm[U]

Out[19]/MatrixForm=

$$\begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \end{pmatrix}$$

Block diagonalization of $E \otimes E$.

In[20]:= **Map[MatrixForm, Table[U.dp[[i]].Transpose[U], {i, 1, 6}]] // FullSimplify**

$$\text{Out[20]} = \left\{ \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -(-1)^{1/3} & 0 \\ 0 & 0 & 0 & \frac{1}{2}i(i+\sqrt{3}) \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & \frac{1}{2}i(i+\sqrt{3}) & 0 \\ 0 & 0 & 0 & -(-1)^{1/3} \end{pmatrix}, \right.$$

$$\left. \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2}i(i+\sqrt{3}) \\ 0 & 0 & -(-1)^{1/3} & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & -(-1)^{1/3} \\ 0 & 0 & \frac{1}{2}i(i+\sqrt{3}) & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \right\}$$

Figure 5.15 Block diagonalization of the direct product representation $E \otimes E$ of the point group C_{3v} . The representation matrices ΓE and the CLEBSCH–GORDAN coefficients $cg1$, $cg2$ and $cg3$ were calculated in Figure 5.14.

5.6**WIGNER–ECKART Theorem**

In the following, the transformation behavior of operators is discussed. The goal is the formulation of the theorem of WIGNER and ECKART which plays an important role, for example, in the discussion of transition probabilities between quantum mechanical states.

Definition 32 (Irreducible tensor operator for coordinate transformations). Let Γ^p be a l_p -dimensional irreducible representation of the group $\mathcal{G}$ with elements $T \in \mathcal{G}$. A set of l_p linear operators $\hat{Q}_1^p, \hat{Q}_2^p, \dots, \hat{Q}_{l_p}^p$ is called a set of irreducible tensor operators of the irreducible representation Γ^p , if for any coordinate transformation $\hat{P}(T)$ the following equation holds

$$\hat{P}(T) \hat{Q}_j^p \hat{P}(T)^{-1} = \sum_{k=1}^{l_p} \Gamma_{kj}^p(T) \hat{Q}_k^p. \quad (5.105)$$

In quantum mechanics, the calculation of matrix elements of linear operators plays a central role, e.g., calculating matrix elements $(\phi_n, \hat{H} \phi_n)$ over the Hamiltonian $\hat{H}$ using eigenfunctions ϕ_n will give the energy eigenvalues of the system under consideration. The following technical lemma will help to prove the WIGNER–ECKART Theorem, which can be used to simplify the calculation of such matrix elements.

Theorem 26 (Technical lemma). Suppose Γ^p, Γ^q and Γ^r are irreducible representations of the finite group $\mathcal{G}$, then the following equation holds,

$$\frac{d_r}{g} \sum_{T \in \mathcal{G}} \Gamma^p(T)_{sj} \Gamma^q(T)_{tk} \Gamma^r(T)_{ul}^* = \sum_{\alpha=1}^{n_r} \begin{pmatrix} p & q & r \\ s & t & u \end{pmatrix} \begin{pmatrix} r & \alpha \\ l & \alpha \end{pmatrix} \begin{pmatrix} p & q \\ j & k \end{pmatrix}, \quad (5.106)$$

where n_r denotes the number of times Γ^r occurs within the direct product representation $\Gamma^p \otimes \Gamma^q$.

Proof. It is assumed that ϕ_j^p and ϕ_k^q are the basis functions of Γ^p and Γ^q , respectively. The basis functions of the direct product representation $\Gamma^p \otimes \Gamma^q \simeq n_1 \Gamma^1 \oplus n_2 \Gamma^2 \oplus \dots$ are denoted by $\psi_l^{r,\alpha}$. By applying the projection operator $\hat{P}_{ul}^r = \sum_{T \in \mathcal{G}} \Gamma^r(T)_{ul}^* \hat{P}(T)$ to the product function $\phi_j^p \phi_k^q$ and using equations (5.91) and (5.93) one obtains

$$\begin{aligned} \hat{P}_{ul}^r \phi_j^p(\mathbf{r}) \phi_k^q(\mathbf{r}) &= \sum_{\alpha=1}^{n_r} \begin{pmatrix} r & \alpha \\ l & \alpha \end{pmatrix} \begin{pmatrix} p & q \\ j & k \end{pmatrix} \psi_u^{r,\alpha}(\mathbf{r}) \\ &= \sum_{s=1}^{l_p} \sum_{t=1}^{l_q} \sum_{\alpha=1}^{n_r} \begin{pmatrix} r & \alpha \\ l & \alpha \end{pmatrix} \begin{pmatrix} p & q \\ j & k \end{pmatrix} \begin{pmatrix} p & q & r \\ s & t & u \end{pmatrix} \phi_s^p(\mathbf{r}) \phi_t^q(\mathbf{r}). \end{aligned} \quad (5.107)$$

Furthermore, it follows from the definition of basis functions that

$$\hat{P}(T) \phi_j^p = \sum_{s=1}^{l_p} \Gamma_{sj}^p(T) \phi_s^p \quad (5.108)$$

and

$$\hat{P}(T) \phi_k^q = \sum_{t=1}^{l_q} \Gamma_{tk}^q(T) \phi_t^q. \quad (5.109)$$

Incorporating the definition of the projection operator gives

$$\hat{P}_{ul}^r \phi_j^p(\mathbf{r}) \phi_k^q(\mathbf{r}) = \sum_{T \in \mathcal{G}} \sum_{s=1}^{l_p} \sum_{t=1}^{l_q} \Gamma^p(T)_{sj} \Gamma^q(T)_{tk} \Gamma^r(T)_{ul}^* \phi_s^p(\mathbf{r}) \phi_t^q(\mathbf{r}). \quad (5.110)$$

Comparison of (5.107) and (5.110) proves the theorem. $\square$

Theorem 27 (The WIGNER–ECKART Theorem). *Let Γ^p , Γ^q , and Γ^r be irreducible representations of a finite group of coordinate transformations $\mathcal{G}$, with dimensions l_p , l_q , and l_r , respectively. Suppose that ϕ_j^p , $j = 1, \dots, l_p$ and ϕ_l^r , $l = 1, \dots, l_r$ are basis functions of the irreducible representations Γ^p and Γ^r . If the operators $\hat{Q}_k^q$, $k = 1, \dots, l_q$ are irreducible tensor operators of Γ^q , then the matrix elements $(\phi_l^r, \hat{Q}_k^q \phi_j^p)$ can be calculated by*

$$\left(\phi_l^r, \hat{Q}_k^q \phi_j^p \right) = \sum_{\alpha=1}^{n_r} \left(\begin{matrix} p & q \\ j & k \end{matrix} \middle| \begin{matrix} r & \alpha \end{matrix} \right)^* \left(r | \hat{Q}^q | p \right)_\alpha. \quad (5.111)$$

The quantity $(r | \hat{Q}^q | p)_\alpha$ is called the reduced matrix element.

Proof. The operator of a coordinate transformation $\hat{P}(T)$ is a unitary operator, i.e., $(f(\mathbf{r}), g(\mathbf{r})) = (\hat{P}(T)f(\mathbf{r}), \hat{P}(T)g(\mathbf{r}))$ for any two functions f and g . Therefore, one can write

$$\begin{aligned} \left(\phi_l^r, \hat{Q}_k^q \phi_j^p \right) &= \left(\hat{P}(T) \phi_l^r, \hat{P}(T) \hat{Q}_k^q \hat{P}(T)^{-1} \hat{P}(T) \phi_j^p \right) \\ &= \sum_{u=1}^{l_r} \sum_{t=1}^{l_q} \sum_{s=1}^{l_p} \Gamma^r(T)_{ul}^* \Gamma^q(T)_{tk} \Gamma^p(T)_{sj} \left(\phi_u^r, \hat{Q}_t^q \phi_s^p \right). \end{aligned} \quad (5.112)$$

Substituting T by T^{-1} , assuming that the irreducible representations are unitary $\underline{\Gamma}^i(T^{-1}) = \underline{\Gamma}^i(T)^\dagger$ and summing over all elements T gives

$$g \left(\phi_l^r, \hat{Q}_k^q \phi_j^p \right) = \sum_{u=1}^{l_r} \sum_{t=1}^{l_q} \sum_{s=1}^{l_p} \sum_{T \in \mathcal{G}} \Gamma^r(T)_{lu} \Gamma^q(T)_{kt}^* \Gamma^p(T)_{js}^* \left(\phi_u^r, \hat{Q}_t^q \phi_s^p \right). \quad (5.113)$$

Now, Theorem 26 can be used to rewrite equation (5.113),

$$\begin{aligned} \left(\phi_l^r, \hat{Q}_k^q \phi_j^p \right) &= \\ &= \sum_{\alpha=1}^{d_r} \left(\begin{matrix} p & q \\ j & k \end{matrix} \middle| \begin{matrix} r & \alpha \end{matrix} \right)^* \frac{1}{d_r} \sum_{s=1}^{l_p} \sum_{t=1}^{l_q} \sum_{u=1}^{l_r} \left(\begin{matrix} r & \alpha \\ u & s \end{matrix} \middle| \begin{matrix} p & q \\ s & t \end{matrix} \right)^* \left(\phi_u^r, \hat{Q}_t^q \phi_s^p \right). \end{aligned} \quad (5.114)$$

The theorem follows by introducing the reduced matrix element $(r | \hat{Q}^q | p)_\alpha$ by

$$(r | \hat{Q}^q | p)_\alpha = \frac{1}{d_r} \sum_{s=1}^{l_p} \sum_{t=1}^{l_q} \sum_{u=1}^{l_r} \left(\begin{matrix} r & \alpha \\ u & s \end{matrix} \middle| \begin{matrix} p & q \\ s & t \end{matrix} \right)^* \left(\phi_u^r, \hat{Q}_t^q \phi_s^p \right). \quad (5.115)$$

$\square$

By applying the WIGNER–ECKART Theorem the numerical effort for calculating a large amount of matrix elements $(\phi_l^r, \hat{Q}_k^q \phi_j^p)$ is decreased, because only one matrix element, e.g., $(\phi_u^r, \hat{Q}_t^q \phi_s^p)$ has to be calculated for a certain combination of irreducible representations. Afterwards, the reduced matrix elements $(r|\hat{Q}^q|p)_\alpha$ can be derived from equation (5.115). All other matrix elements are calculated from the CLEBSCH–GORDAN coefficients, which can be obtained algebraically. Furthermore, from the CLEBSCH–GORDAN coefficients (i.e., from the symmetry of the system under consideration) it is possible to estimate all matrix elements $(\phi_l^r, \hat{Q}_k^q \phi_j^p)$ that have to be zero.

5.7

Induced Representations

In the following, the technique of induced representations is introduced. The results of this section are kept as short as possible and concentrate on what is necessary to construct the irreducible representations of symmorph space groups explained in Section 6.4. The idea is to construct a matrix representation Γ of a group $\mathcal{G}$ from an already known representation Γ_S of a subgroup $S \subset \mathcal{G}$.

Let s denote the order of the subgroup S and g the order of $\mathcal{G}$. Then, according to Section 3.2.2, it is possible to construct $M = g/s$ right cosets. Let T_i denote the coset representatives, then it is possible to write $\mathcal{G}$ as

$$\mathcal{G} = ST_1 + ST_2 + \dots + ST_M. \quad (5.116)$$

Theorem 28 (Induction of representations). *Let S be a subgroup of $\mathcal{G}$ and $T_1, \dots, T_M$ be $M = g/s$ coset representatives for the decomposition of $\mathcal{G}$ into right cosets with respect to S , where g and s denote the orders of S and $\mathcal{G}$, respectively. Then it is possible to construct an Md -dimensional unitary representation Γ for $\mathcal{G}$ from a d -dimensional unitary representation Γ_S of S via*

$$\Gamma(T)_{kt,jr} = \begin{cases} \Gamma_S \left(T_k T T_j^{-1} \right)_{tr}, & \text{if } T_k T T_j^{-1} \in S \\ 0, & \text{if } T_k T T_j^{-1} \notin S \end{cases}. \quad (5.117)$$

Proof. The theorem follows from verifying that the representation matrices of the induced representation have to fulfill $\underline{\Gamma}(T_1)\underline{\Gamma}(T_2) = \underline{\Gamma}(T_1 T_2)$. The product is calculated via

$$(\underline{\Gamma}(T_1)\underline{\Gamma}(T_2))_{kt,jr} = \sum_{l=1}^M \sum_{p=1}^d \Gamma(T_1)_{kt,lp} \Gamma(T_2)_{lp,jr}. \quad (5.118)$$

Nonzero contributions within the sum only occur when $T_k T_1 T_l^{-1} \in S$ and $T_l T_2 T_j^{-1} \in S$. However, $T_k T_1 T_l^{-1} \in S$ if and only if $T_k T_1$ is an element of

the right coset ST_l . Since $T_k T_1$ is fixed, at most only one l can lead to a non-zero contribution. Let's denote this particular index by l' . Since $(T_k T_1 T_2 T_j^{-1}) = (T_k T_1 T_{l'}^{-1})(T_{l'} T_2 T_j^{-1})$ it follows that $(T_{l'} T_2 T_j^{-1}) \in S$ if and only if $(T_k T_1 T_2 T_j^{-1}) \in S$. In this case it is possible to write

$$\sum_{p=1}^d \Gamma_S (T_k T_1 T_{l'}^{-1})_{tp} \Gamma_S (T_{l'} T_2 T_j^{-1})_{pr} = \Gamma_S (T_k T_1 T_2 T_j^{-1})_{tr} . \quad (5.119)$$

Hence, it follows to write

$$\sum_{l=1}^M \sum_{p=1}^d \Gamma(T_1)_{kt,lp} \Gamma(T_2)_{lp,jr} = \begin{cases} \Gamma_S (T_k T_1 T_2 T_j^{-1})_{tr} , & \text{if } T_k T_1 T_2 T_j^{-1} \in S \\ 0 , & \text{if } T_k T_1 T_2 T_j^{-1} \notin S \end{cases} . \quad (5.120)$$

□

For a representation Γ of $\mathcal{G}$ that was induced from Γ_S of S it will be written

$$\Gamma = \Gamma_S \uparrow \mathcal{G} \quad (5.121)$$

in the following. The characters of the induced representation Γ can be calculated by taking the trace in equation (5.117),

$$\chi(T) = \sum_{\langle j \rangle} \chi_S (T_j T T_j^{-1}) , \quad (5.122)$$

where $\langle j \rangle$ denotes that the sum is over all coset representatives with the property $T_j T T_j^{-1} \in S$ and χ_S denotes the characters of Γ_S .

According to Section 4.2.2, the group of all pure lattice translations $\mathcal{T}$ is an invariant subgroup of a crystallographic space group. Furthermore, $\mathcal{T}$ is Abelian, because all translations commute. For the symmorphic space groups, the space group can be written as the semidirect product of $\mathcal{T}$ with a crystallographic point group.

In the following, the special case of a group $\mathcal{G}$ being the semidirect product of an Abelian invariant subgroup $\mathcal{A}$ and a subgroup $\mathcal{B}$ will be discussed,

$$\mathcal{G} = \mathcal{A} \rtimes \mathcal{B} . \quad (5.123)$$

The orders of the two groups are denoted by a and b ,

$$a = \text{ord}(\mathcal{A}) , \quad b = \text{ord}(\mathcal{B}) . \quad (5.124)$$

Since $\mathcal{A}$ is an Abelian group it has a classes and a one-dimensional inequivalent irreducible representations $\Gamma_{\mathcal{A}}^q$, $q = 1, \dots, a$. Let $\chi_{\mathcal{A}}^q(A)$ denote the character of an element $A \in \mathcal{A}$ within the irreducible representation $\Gamma_{\mathcal{A}}^q$.

Definition 33 (The little group). *The subset $\mathcal{B}(q) \subset \mathcal{B}$ containing all elements $B \in \mathcal{B}$ with the property*

$$\chi_{\mathcal{A}}^q(BAB^{-1}) = \chi_{\mathcal{A}}^q(A), \quad \text{for all } A \in \mathcal{A} \quad (5.125)$$

is called the little group of q (with respect to $\mathcal{A}$).

Example 34 (Little group). To illustrate the concept of the little group we consider the group D_4 as a semidirect product of C_4 with principal axis z and C_2 with principal axis x ,

$$D_4 = \{E, C_{2z}, C_{4z}, C_{4z}^{-1}\} \rtimes \{E, C_{2x}\}. \quad (5.126)$$

Since C_4 is a cyclic and Abelian group it has four irreducible representations, as can be seen in Figure 5.16. The elements of C_4 exhibit the following transformation properties under C_{2x} ,

$$C_{2x} E C_{2x}^{-1} = E, \quad C_{2x} C_{2z} C_{2x}^{-1} = C_{2z}, \quad (5.127)$$

$$C_{2x} C_{4z} C_{2x}^{-1} = C_{4z}^{-1}, \quad C_{2x} C_{4z}^{-1} C_{2x}^{-1} = C_{4z}. \quad (5.128)$$

For the first irreducible representation Γ^1 , with

$$\chi^1(E) = \chi^1(C_{2z}) = \chi^1(C_{4z}) = \chi^1(C_{4z}^{-1}) = 1, \quad (5.129)$$

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```
In[19]:= c4 = GTInstallGroup[C4]
```

The standard representation has changed to 0(3)

```
Out[19]:= {Ee, C2z, C4z^1, C4z}
```

```
In[20]:= GTCharacterTable[c4];
```

	Ee	C2z	C4z ¹	C4z
Γ^1	1	1	1	1
Γ^2	1	-1	-i	i
Γ^3	1	-1	i	-i
Γ^4	1	1	-1	-1

$C_1 = \{Ee\}$

$C_2 = \{C_{2z}\}$

$C_3 = \{C_{4z}^1\}$

$C_4 = \{C_{4z}\}$

Figure 5.16 Character table of C_4 .

it follows that the little group is given by the whole group C_2 , $\mathcal{B}(1) = C_2$. However, since the character for C_{4z} is different from the character of C_{4z}^{-1} for all the other irreducible representations, it follows that $\mathcal{B}(2) = \mathcal{B}(3) = \mathcal{B}(4) = \{E\}$.

Task 21 (The little group). Become familiar with the concept of the little group by repeating the example above for the group D_{4h} , given by

$$D_{4h} = \{E, C_{2z}, C_{4z}, C_{4z}^{-1}\} \rtimes \{E, C_{2x}, IE, IC_{2x}\}. \quad (5.130)$$

Let $b(q) = \text{ord}(\mathcal{B}(q))$ in the following. Because $\mathcal{B}(q)$ is a subgroup of $\mathcal{B}$, it is possible to obtain $M(q) = b/b(q)$ right cosets of $\mathcal{B}$ with respect to $\mathcal{B}(q)$,

$$\mathcal{B} = \mathcal{B}(q)B_1 + \mathcal{B}(q)B_2 + \cdots + \mathcal{B}(q)B_{M(q)}, \quad (5.131)$$

where $B_1, \dots, B_{M(q)}$ denote the coset representatives.

In a similar manner to (5.125), it is possible to define a map $\mathcal{B}(q)$ of the integers $q = 1, \dots, a$ to itself, by fixing a $B \in \mathcal{B}$ and writing

$$\chi_{\mathcal{A}}^{B(q)}(A) = \chi_{\mathcal{A}}^q(B^{-1}AB), \quad \text{for all } A \in \mathcal{A}. \quad (5.132)$$

However, since every element B can be written as a product $B'B_j$, where $B' \in \mathcal{B}(q)$ and B_j is one of the coset representatives in (5.131), it can be verified that only $M(q)$ inequivalent maps $B_1(q), \dots, B_{M(q)}(q)$ can be found,

$$\chi_{\mathcal{A}}^{B(q)}(A) = \chi_{\mathcal{A}}^q(BAB^{-1}) \quad (5.133)$$

$$= \chi_{\mathcal{A}}^q \left((B'B_j) A (B'B_j)^{-1} \right) \quad (5.134)$$

$$= \chi_{\mathcal{A}}^q \left(B_j A B_j^{-1} \right) \quad (5.135)$$

$$= \chi_{\mathcal{A}}^{B_j(q)}(A). \quad (5.136)$$

Definition 34 (Orbit of q). The set of $M(q)$ integers $\{B_1(q), \dots, B_{M(q)}(q)\}$ is called the orbit of q .

Theorem 29 (Isomorphism of little groups). All $M(q)$ groups $\mathcal{B}(B_j(q))$ within the orbit of q are isomorphic to $\mathcal{B}(q)$.

Proof. Per definition the group $\mathcal{B}(B_j(q))$ is a little group and has the property

$$\chi_{\mathcal{A}}^{B_j(q)}(BAB^{-1}) = \chi_{\mathcal{A}}^{B_j(q)}(A), \quad \text{for all } A \in \mathcal{A} \quad (5.137)$$

with $B \in \mathcal{B}(B_j(q)) \subset \mathcal{B}$. Using (5.125) the above equation can be rewritten as

$$\chi_{\mathcal{A}}^q \left(B_j B A B^{-1} B_j^{-1} \right) = \chi_{\mathcal{A}}^q \left(B_j A B_j^{-1} \right), \quad \text{for all } A \in \mathcal{A}. \quad (5.138)$$

It is possible to define an automorphism $\phi : \mathcal{G} \rightarrow \mathcal{G}$ via

$$\phi(T) = B_j T B_j^{-1}. \quad (5.139)$$

Clearly, (5.139) defines a map from $\mathcal{G}$ to itself. However, since $\mathcal{A}$ is an invariant subgroup it also provides a map from $\mathcal{A}$ to itself. By writing $A = B_j^{-1} A' B_j$, equation (5.138) can be rewritten as

$$\chi_{\mathcal{A}}^q \left(\left(B_j B B_j^{-1} \right) A' \left(B_j B B_j^{-1} \right)^{-1} \right) = \chi_{\mathcal{A}}^q(A'), \quad \text{for all } A' \in \mathcal{A}. \quad (5.140)$$

Hence, it is possible to identify that $\phi_j(B) = B_j B B_j^{-1}$ maps $B(B_j(q))$ to $B(q)$. Since ϕ_j is isomorphic the groups $B(B_j(q))$ and $B(q)$ have to be isomorphic. $\square$

In the last step, a subgroup of $\mathcal{G} = \mathcal{A} \rtimes \mathcal{B}$ is needed for which it is possible to calculate the representation matrices easily. From there the method of induction can be applied. Such a subgroup is given by

$$S(q) = \mathcal{A} \rtimes B(q). \quad (5.141)$$

It contains all products AB with $A \in \mathcal{A}$ and $B \in B(q)$. Since $\mathcal{A}$ is an invariant subgroup of $\mathcal{G}$ and $B \in \mathcal{G}$ in general, there exists a relation

$$A' = B^{-1} A'' B, \quad \text{for all } A' \in \mathcal{A}, \quad (5.142)$$

with $A'' \in \mathcal{A}$ and $B \in B(q)$. Hence, the product of two elements AB and $A'B'$ of $S(q)$ can be written as

$$ABA'B' = ABB^{-1}A''BB' = AA''BB' \in S(q). \quad (5.143)$$

Theorem 30 (Irreducible representations of $S(q)$). *Let $\Gamma_{B(q)}^p$ be a l_p -dimensional unitary irreducible representation of $B(q)$. Then, the set of $l_p \times l_p$ -dimensional matrices $\underline{\Gamma}_{S(q)}^{q,p}$ given by*

$$\underline{\Gamma}_{S(q)}^{q,p}(AB) = \chi_{\mathcal{A}}^q(A) \underline{\Gamma}_{B(q)}^p(B) \quad (5.144)$$

form a unitary representation of the group $S(q)$, denoted by $\Gamma_{S(q)}^{q,p}$.

Proof.

$$\underline{\Gamma}_{S(q)}^{q,p}((AB)(A'B')) = \underline{\Gamma}_{S(q)}^{q,p}(AA''BB') \quad (5.145)$$

$$= \chi_{\mathcal{A}}^q(AA'') \underline{\Gamma}_{B(q)}^p(BB') \quad (5.146)$$

$$= \chi_{\mathcal{A}}^q(A) \chi_{\mathcal{A}}^q(A') \underline{\Gamma}_{B(q)}^p(B) \underline{\Gamma}_{B(q)}^p(B') \quad (5.147)$$

$$= \underline{\Gamma}_{S(q)}^{q,p}(AB) \underline{\Gamma}_{S(q)}^{q,p}(A'B'). \quad (5.148)$$

$\square$

The only thing that remains to verify is the decomposition of $\mathcal{G}$ into right cosets with respect to $S(q)$. The following theorem helps to clarify.

Theorem 31 (Coset representations of $S(q)$). *Let $B_1, \dots, B_{M(q)}$ be $M(q) = b/b(q)$ coset representatives of the decomposition of $\mathcal{B}$ into right cosets with respect to $\mathcal{B}(q)$ and $b = \text{ord}(\mathcal{B})$ as well as $b(q) = \text{ord}(\mathcal{B}(q))$. Then $B_1, \dots, B_{M(q)}$ also serve as coset representatives of the decomposition of $\mathcal{G}$ into right cosets with respect to $S(q)$.*

Proof. For finite $\mathcal{A}$ the number of right cosets of $\mathcal{G}$ with respect to $S(q)$ is given by

$$g/s(q) = ab/(ab(q)) = b/b(q) = M(q). \quad (5.149)$$

Furthermore, the sets $S(q)B_i$ and $S(q)B_j$ can only be distinct if $\mathcal{B}(q)B_i$ and $\mathcal{B}(q)B_j$ are distinct. Let's prove that by contradiction. Assume that $S(q)B_i$ and $S(q)B_j$ have a common element. That means it is possible to find $A, A' \in \mathcal{A}$ and $B, B' \in \mathcal{B}(q)$ such that

$$ABB_i = A'B'B_j. \quad (5.150)$$

Since $S(q) = \mathcal{A} \rtimes \mathcal{B}(q)$ it follows that $A = A'$ and thus $BB_j = B'B_k$. Hence, it follows that $\mathcal{B}(q)B_i$ and $\mathcal{B}(q)B_j$ possess a common element, which is in contradiction to B_i and B_j being different coset representatives. $\square$

Finally, a unitary representation of the group $S(q)$ is known together with the coset representatives of the decomposition of $\mathcal{G}$ into right cosets with respect to $S(q)$. Hence, equation (5.117) can be applied to calculate representation matrices by the method of induction,

$$\Gamma^{q,p}_{S(q)} = \Gamma^{q,p}_{S(q)} \uparrow \mathcal{G}. \quad (5.151)$$

The following theorem summarizes the derivations of this section.

Theorem 32 (Irreducible representations of semidirect product groups). *Let $\mathcal{G}$ be a semidirect product group $\mathcal{G} = \mathcal{A} \rtimes \mathcal{B}$ and $\mathcal{A}$ an Abelian invariant subgroup of $\mathcal{G}$. Let $B_1, \dots, B_{M(q)}$ be $M(q)$ coset representatives of the decomposition of $\mathcal{B}$ into right cosets with respect to $\mathcal{B}(q)$. Then, a unitary representation $\Gamma^{q,p}$ of $\mathcal{G}$ can be induced from the unitary irreducible representations $\Gamma^p_{\mathcal{B}(q)}$ of $\mathcal{B}(q)$ and $\Gamma^q_{\mathcal{A}}$ of $\mathcal{A}$, via*

$$\Gamma^{q,p}(AB)_{kt,jr} = \begin{cases} \chi_{\mathcal{A}}^{B_k(q)}(A) \Gamma^p_{\mathcal{B}(q)}(B_k B B_j^{-1})_{tr}, & \text{if } B_k B B_j^{-1} \in \mathcal{B}(q) \\ 0, & \text{if } B_k B B_j^{-1} \notin \mathcal{B}(q) \end{cases}. \quad (5.152)$$

Furthermore, this representation has the following properties:

1. $\Gamma^{q,p}$ is an irreducible representation of $\mathcal{G}$
2. all unitary irreducible representations of $\mathcal{G}$ can be obtained by choosing one value of q in each orbit and constructing $\Gamma^{q,p}$ for each inequivalent irreducible representation $\Gamma^p_{\mathcal{B}(q)}$ of $\mathcal{B}(q)$.

Proof. Equation (5.152) can be derived by following the derivations throughout this section. The statements about irreducible representations are omitted for reasons of brevity. A full proof can be found, e.g., in [36]. $\square$

As mentioned at the beginning of this section, the theory of induced representations can be nicely applied, e.g., for the construction of the irreducible representations of the symmorphic space groups. However, to make the content a bit more accessible an example for the finite group O_h will be given in the following.

Example 35 (The irreducible representations of O_h). As an example to verify the concept of induced representations, the group of the octahedron O_h is discussed in the following. It contains 48 elements, as can be seen in Figure 5.17. Alternatively, it can be written as the semidirect product

$$O_h = C_i \rtimes T_d, \quad (5.153)$$

where $C_i = \{Ee, IEe\}$. According to Figure 5.18, C_i has two one-dimensional irreducible representations A_g and A_u , where A_g is even and A_u is odd with respect to the inversion. T_d has five irreducible representations. These are the two one-dimensional representations A_1 and A_2 , the two-dimensional representation E , and the two three-dimensional representations T_1 and T_2 . Since $BAB^{-1} = A$ for all elements $A \in C_i$ and $B \in T_d$, the little groups of both A_g and A_u are given by the entire group T_d (see Definition 33). Therefore, it follows $M(A_g) = M(A_u) = 1$. Similarly, it follows that $S(A_g) = S(A_u) = C_i \rtimes T_d = O_h$. Hence, according to Theorem 31 and Theorem 32 one can write

$$\underline{\Gamma}_{O_h}^{q,p}(AB) = \chi_{C_i}^q(A) \underline{\Gamma}_{T_d}^p(B). \quad (5.154)$$

It follows that O_h has ten irreducible representations, where the representation matrices of the five irreducible representations of T_d are multiplied with a prefactor $\pm$ according to the representations A_g and A_u of C_i for all elements $IEeB$ with $B \in T_d$. As can be seen in Figure 5.18, the nomenclature of the irreducible representations of O_h are a mixture of the denotations of T_d and C_i .

Mathematica

GTProductGroup

The group O_h has 48 elements.

```
In[9]:= oh = GTInstallGroup[Oh]
```

The standard representation has changed to $O(3)$

```
Out[9]:= {Ee, C2z, C2f, C2e, C2y, C2b, C2d, C2c, C2a, C2x, C3β, C3γ, C3γ-1, C3α-1, C3β-1, C3δ-1, C3α, C3δ, C4z-1, C4y, C4y-1, C4z, C4x-1, C4x, IEe, IC2x, IC2a, IC2c, IC2d, IC2b, IC2y, IC2e, IC2f, IC2z, IC4x, IC4x-1, IC4z, IC4y-1, IC4y, IC4z-1, IC3δ, IC3α, IC3δ-1, IC3β-1, IC3α-1, IC3γ-1, IC3γ, IC3β}
```

```
In[10]:= GTGroupOrder[oh]
```

Order of the group: 48

```
Out[10]:= 48
```

The group T_d has 24 elements.

```
In[11]:= td = GTInstallGroup[Td]
```

The standard representation has changed to $O(3)$

```
Out[11]:= {Ee, C2z, C2y, C2x, C3β, C3γ, C3γ-1, C3α-1, C3β-1, C3δ-1, C3α, C3δ, IC2a, IC2c, IC2d, IC2b, IC2e, IC2f, IC4x, IC4x-1, IC4z, IC4y-1, IC4y, IC4z-1}
```

```
In[12]:= GTGroupOrder[td]
```

Order of the group: 24

```
Out[12]:= 24
```

The group C_i has 2 elements.

```
In[13]:= ci = GTInstallGroup[Ci]
```

The standard representation has changed to $O(3)$

```
Out[13]:= {Ee, IEe}
```

```
In[14]:= GTGroupOrder[ci]
```

Order of the group: 2

```
Out[14]:= 2
```

Alternatively, O_h can be written as the semi-direct product of C_i and T_d .

```
In[15]:= GTProductGroup[ci, td]
```

semi-direct product

```
Out[15]:= {IEe, C2z, C2f, IC4x, IC4x-1, C2e, C2y, IC2x, C2b, IC2a, IC3δ, C3β, C3γ, IC3α, IC4z, C4z-1, IC3δ-1, C3γ-1, C2d, IC2c-1, IC2c, C4y, C3α-1, IC3β-1, C3β-1, IC3α-1, IC4y, C2c, C4y-1, IC2d, IC3γ-1, C3δ-1, IC4z-1, C4z, C3α, IC3γ, IC3β, C3δ, C2a, IC2b, C2x, IC2y, IC2e, C4x-1, C4x, IC2f, IC2z, Ee}
```

Figure 5.17 The point group O_h can be written as the semidirect product $C_i \rtimes T_d$.

Mathematica

GTCharacterTable

The character table of C_2 :

```
In[16]=GTCharacterTable[ci, GOirepNotation -> "Mulliken"];
```

	Ee	IEe
A_1	1	1
A_2	1	-1

$C_1 = \{Ee\}$

$C_2 = \{IEe\}$

The character table of T_d :

```
In[17]=GTCharacterTable[td, GOirepNotation -> "Mulliken"];
```

	Ee	3 C_{2z}	6 IC_{4x}	6 IC_{2a}	8 C_{3b}
A_1	1	1	1	1	1
A_2	1	1	-1	-1	1
E	2	2	0	0	-1
T_2	3	-1	-1	1	0
T_1	3	-1	1	-1	0

$C_1 = \{Ee\}$

$C_2 = \{C_{2x}, C_{2y}, C_{2z}\}$

$C_3 = \{IC_{4x}, IC_{4y}, IC_{4z}, IC_{4x}^{-1}, IC_{4y}^{-1}, IC_{4z}^{-1}\}$

$C_4 = \{IC_{2a}, IC_{2c}, IC_{2d}, IC_{2b}, IC_{2e}, IC_{2f}\}$

$C_5 = \{C_{3b}, C_{3y}, C_{3y}^{-1}, C_{3a}^{-1}, C_{3b}^{-1}, C_{3a}^{-1}, C_{3a}, C_{3b}\}$

The character table of O_h :

```
In[18]=GTCharacterTable[oh, GOirepNotation -> "Mulliken"];
```

	Ee	3 C_{2z}	3 IC_{2K}	6 C_{2f}	6 IC_{4K}	6 IC_{2a}	6 C_{4z}^{-1}	8 IC_{3b}	8 C_{3b}	IEe
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	-1	1	-1
A_{1u}	1	1	-1	1	-1	-1	1	-1	1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	1	1	1
E_g	2	2	-2	0	0	0	0	1	-1	-2
E_u	2	2	2	0	0	0	0	-1	-1	2
T_{1g}	3	-1	-1	-1	1	-1	1	0	0	3
T_{2g}	3	-1	-1	1	-1	1	-1	0	0	3
T_{1u}	3	-1	1	-1	-1	1	1	0	0	-3
T_{2u}	3	-1	1	1	1	-1	-1	0	0	-3

$C_1 = \{Ee\}$

$C_2 = \{C_{2x}, C_{2y}, C_{2z}\}$

$C_3 = \{IC_{2x}, IC_{2y}, IC_{2z}\}$

$C_4 = \{C_{2f}, C_{2e}, C_{2b}, C_{2d}, C_{2c}, C_{2a}\}$

$C_5 = \{IC_{4x}, IC_{4x}^{-1}, IC_{4y}, IC_{4y}^{-1}, IC_{4z}, IC_{4z}^{-1}\}$

$C_6 = \{IC_{2a}, IC_{2c}, IC_{2d}, IC_{2b}, IC_{2e}, IC_{2f}\}$

$C_7 = \{C_{4z}^{-1}, C_{4y}, C_{4y}^{-1}, C_{4z}, C_{4x}^{-1}, C_{4x}\}$

$C_8 = \{IC_{3b}, IC_{3a}, IC_{3b}^{-1}, IC_{3b}^{-1}, IC_{3a}^{-1}, IC_{3y}, IC_{3y}, IC_{3b}\}$

$C_9 = \{C_{3b}, C_{3y}, C_{3y}^{-1}, C_{3a}^{-1}, C_{3b}^{-1}, C_{3b}^{-1}, C_{3a}, C_{3b}\}$

$C_{10} = \{IEe\}$

Figure 5.18 The character tables of C_2 , T_d and O_h .

6

Symmetry and Representation Theory in k-Space

Die moderne Physik schreitet also auf denselben geistigen Wegen voran, auf denen schon die Pythagoreer und Plato gewandelt sind, und es sieht so aus, als werde am Ende dieses Weges eine sehr einfache Formulierung der Naturgesetze stehen, so einfach, wie auch Plato sie sich erhofft hat.

Werner Heisenberg (Physik und Philosophie, Stuttgart, 2006)

Throughout this chapter the representation theory for space groups is established. To do so, the concept of the **k**-space is introduced. The wave-vector **k** represents a quantum number which is a consequence of the translational invariance in lattice periodic systems. As the **k**-space is lattice periodic, it suffices in most cases to concentrate on the electronic states represented by **k**-vectors within a minimal cell, the so called BRILLOUIN zone. In general, irreducible representations of space groups can be successively calculated by induction as soon as the irreducible representations of a normal subgroup are known. As the group of pure lattice translations is a normal subgroup where the irreducible representations can be calculated analytically, it can be used as a starting point. A specific simplification occurs in the case of symmorphic space groups, where the group can be written as the semidirect product of a point group containing pure rotations and the translation group of the lattice.

6.1

The Cyclic BORN-VON KÁRMÁN Boundary Condition and the BLOCH Wave

In the following, the solution of the SCHRÖDINGER equation

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \phi(\mathbf{r}) = E \phi(\mathbf{r}), \quad (6.1)$$

for a crystalline solid with the periodic potential

$$V(\mathbf{r} + \mathbf{t}_n) = V(\mathbf{r}) \quad (6.2)$$

will be discussed. A more general discussion of the SCHRÖDINGER equation will follow in the next chapter. Analogously to Section 4.2.2, $\mathbf{t}_n$ denotes a primitive lattice vector. Intuitively, physical quantities like the electron density should reflect the periodicity of the potential. The properties of the wave function as a complex quantity within a periodic potential is derived subsequently.

Definition 35 (BORN–VON KÁRMÁN boundary condition¹⁾). *Let ϕ be a solution of the SCHRÖDINGER equation for a periodic potential. For the three basis vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ of the lattice and sufficiently large integers N_1 , N_2 and N_3 the following boundary condition*

$$\phi(\mathbf{r}) = \phi(\mathbf{r} \pm N_1 \mathbf{a}_1) = \phi(\mathbf{r} \pm N_2 \mathbf{a}_2) = \phi(\mathbf{r} \pm N_3 \mathbf{a}_3), \quad (6.3)$$

is called BORN–VON KÁRMÁN boundary condition.

The BORN–VON KÁRMÁN boundary condition forces the wave function to be periodic within a sufficiently large unit cell. Considering the translational transformations of the wave function along the direction of one of the basis vectors $\mathbf{a}_i$ to be of the form

$$\hat{P}(\{E \mid m\mathbf{a}_i\})\phi(\mathbf{r}) = \phi(\mathbf{r} - m\mathbf{a}_i), \quad (6.4)$$

it follows for $m = N_i$,

$$\hat{P}(\{E \mid N_i \mathbf{a}_i\})\phi(\mathbf{r}) = \phi(\mathbf{r}) = \hat{P}(\{E \mid \mathbf{0}\})\phi(\mathbf{r}), \quad (6.5)$$

where $\{E \mid \mathbf{0}\}$ is the identity element of the space group. Hence, the BORN–VON KÁRMÁN boundary condition induces a finite group $\mathcal{T}^f$ for the pure translations. The combination of the point group symmetry of the crystal ($\mathcal{G}_0$) together with the finite group of translations forms a finite space group $\mathcal{R}^f$. It represents an approximation of the infinite space groups introduced in Section 4.2.2.

Theorem 33 ($\mathcal{T}^f$ is an invariant subgroup of $\mathcal{R}^f$). *The finite translation group $\mathcal{T}^f$ of all lattice translations forms an invariant subgroup of the space group $\mathcal{R}^f$. The quotient group $\mathcal{R}^f/\mathcal{T}^f$ is isomorphic to $\mathcal{G}_0$.*

Proof. The proof is equivalent to the proof of Theorem 12. □

Clearly, $\mathcal{T}^f$ is an Abelian group. Hence, each element forms a class on its own (Section 3.2.1) and the number of classes is equal to the number of group elements. Since translations are commutative, all translation groups are Abelian. According to Theorem 20 the number of irreducible representations is equal to the number of classes. Since the sum of the squares of the dimensions of the irreducible representations has to be equal to the order of the group (Theorem 22) all irreducible representations are one-dimensional.

1) The name refers to the initial work of BORN and VON KÁRMÁN in 1912 [97]. The boundary condition is also referred to as the *cyclic boundary condition* or the *periodic boundary condition*.

Consider a one-dimensional irreducible representation Γ^p and a translation along the basis vector $\mathbf{a}_i$. Then, the 1×1 -dimensional representation matrix is given by a complex number C_i ,

$$\Gamma^p(\{E | \mathbf{a}_i\}) = C_i. \quad (6.6)$$

From (6.5) it follows that $(C_i)^{N_i} = 1$. Hence, C_i has to possess the form

$$C_i = e^{-2\pi i \frac{p_i}{N_i}}, \quad (6.7)$$

where p_i is an integer, having one of the values $0, \dots, N_i - 1$. Considering a general primitive translation within the lattice $\mathbf{t}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$ a representation can be found by writing

$$\Gamma^p(\{\underline{\mathbf{E}} | \mathbf{t}_n\}) = e^{-2\pi i \left(n_1 \frac{p_1}{N_1} + n_2 \frac{p_2}{N_2} + n_3 \frac{p_3}{N_3} \right)}, \quad (6.8)$$

where p denotes the triple (p_1, p_2, p_3) .

Definition 36 (Reciprocal basis). *The set of vectors²⁾ $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ having the property*

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{i,j}. \quad (6.9)$$

is called the reciprocal basis.

By introducing a vector $\mathbf{k}$ via

$$\mathbf{k} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3, \quad k_i = \frac{p_i}{N_i}, \quad (6.10)$$

equation (6.8) can be rewritten as follows,

$$\Gamma^p(\{\underline{\mathbf{E}} | \mathbf{t}_n\}) = e^{-i\mathbf{k} \cdot \mathbf{t}_n} = \Gamma^{\mathbf{k}}(\{\underline{\mathbf{E}} | \mathbf{t}_n\}). \quad (6.11)$$

Hence, for a basis function of the irreducible representation $\Gamma^{\mathbf{k}}$ the transformation under a translation operator can be written as

$$\hat{P}(\{E | \mathbf{t}_n\}) \phi_{\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k} \cdot \mathbf{t}_n} \phi_{\mathbf{k}}(\mathbf{r}) = \phi_{\mathbf{k}}(\mathbf{r} - \mathbf{t}_n). \quad (6.12)$$

Equation (6.12) motivates the BLOCH theorem.

Theorem 34 (BLOCH theorem). *All eigenfunctions of a Hamiltonian describing a crystal can be written as*

$$\phi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}(\mathbf{r}), \quad (6.13)$$

where $u_{\mathbf{k}}$ is a lattice periodic function

$$u_{\mathbf{k}}(\mathbf{r} + \mathbf{t}_n) = u_{\mathbf{k}}(\mathbf{r}). \quad (6.14)$$

2) Here, the 3-dimensional case is discussed. The definition can be generalized to the d -dimensional space using the vectors $\mathbf{b}_1, \dots, \mathbf{b}_d$.

By increasing the size of the BORN–VON KÁRMÁN cell $N_i \rightarrow \infty$, the space of $\mathbf{k}$ -vectors becomes continuous and the eigenvalues $E(\mathbf{k})$ of the corresponding SCHRÖDINGER equation,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \phi_{\mathbf{k}}(\mathbf{r}) = E(\mathbf{k}) \phi_{\mathbf{k}}(\mathbf{r}), \quad (6.15)$$

become a function of $\mathbf{k}$.

6.2

The Reciprocal Lattice

The reciprocal lattice	
GTReciprocalBasis	Calculates the reciprocal basis vectors from the real-space basis vectors

In Definition 36, reciprocal basis vectors were introduced via the relation $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{i,j}$, where $\mathbf{a}_i$ denotes a real-space basis vector and $\mathbf{b}_j$ a reciprocal basis vector. Analogously to the real-space lattice, which can be constructed from the vectors $\mathbf{a}_i$,

$$\mathbf{t}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad (6.16)$$

the reciprocal lattice can be constructed from the reciprocal lattice vectors $\mathbf{b}_i$,

$$\mathbf{K}_m = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3. \quad (6.17)$$

The reciprocal lattice vectors and the real-space lattice vectors fulfill the following relation

$$e^{-i\mathbf{K}_m \cdot \mathbf{t}_n} = 1 \quad (6.18)$$

In three dimensions, the reciprocal basis can be obtained from the real-space basis via

$$\mathbf{b}_i = 2\pi \frac{\mathbf{a}_j \times \mathbf{a}_k}{\mathbf{a}_i \cdot (\mathbf{a}_j \times \mathbf{a}_k)}, \quad (6.19)$$

where (i, j, k) denote one of the cyclic permutations of $(1, 2, 3)$. Equation (6.19) is implemented within the GTPack command **GTReciprocalBasis**.

Example 36 (Reciprocal basis for a monoclinic lattice). As an example, the reciprocal basis vectors for a monoclinic lattice are calculated using GTPack. The real-space basis is given by

$$\mathbf{a}_1 = (a, 0, 0), \quad \mathbf{a}_2 = (0, b, 0), \quad \mathbf{a}_3 = (c \cos(\beta), 0, c \sin(\beta)). \quad (6.20)$$

Mathematica GTReciprocalBasis	
In[9]:=	basis = {{ a , 0, 0}, {0, b , 0}, { c Cos[β], 0, c Sin[β]}}
Out[9]=	{{ a , 0, 0}, {0, b , 0}, { c Cos[β], 0, c Sin[β]}}
In[10]:=	GTReciprocalBasis [basis]
Out[10]=	{{{ $\frac{2\pi}{a}$, 0, $-\frac{2\pi \cot[\beta]}{a}$ }, {0, $\frac{2\pi}{b}$, 0}, {0, 0, $\frac{2\pi \csc[\beta]}{c}$ }}}

Figure 6.1 Calculation of the reciprocal basis for a monoclinic lattice using **GTReciprocalBasis**.

Here, β denotes the angle between $\mathbf{a}_1$ and $\mathbf{a}_3$. By making use of equation (6.19), $\mathbf{b}_1$ can be calculated as follows

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} = \frac{2\pi}{a} \left(1, 0, -\frac{1}{\tan(\beta)} \right) = \frac{2\pi}{a} (1, 0, -\cot(\beta)) . \quad (6.21)$$

Analogously, it can be verified that

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)} = \frac{2\pi}{b} (0, 1, 0) \quad (6.22)$$

and

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)} = \frac{2\pi}{c} \left(0, 0, \frac{1}{\sin(\beta)} \right) = \frac{2\pi}{c} (0, 0, \csc(\beta)) . \quad (6.23)$$

The application of the command **GTReciprocalBasis** within GTPack is shown in Figure 6.1.

Task 22 (Reciprocal lattice of the fcc and bcc lattices). Use the commands **GTBravaisLattice** and **GTReciprocalBasis** to verify that the reciprocal lattice of a face-centered cubic lattice is given by a space-centered lattice and vice versa.

6.3

The BRILLOUIN Zone and the Group of the Wave Vector **k**

The BRILLOUIN zone and the group of the wave vector k	
GTGroupOfK	Computes the group of the wave vector k
GTStarOfK	Computes the star of the wave vector k
GTVoronoiCell	Constructs the BRILLOUIN zone and illustrates high symmetry points and lines
GTBZPath	Gives information about high symmetry points for crystallographic lattices

In Section 4.2.3, the WIGNER–SEITZ cell was introduced as being the unique cell containing only one lattice point by having the property that each point within the interior of the cell is closer to this particular point than to any other lattice point of the crystal. The analogue of the WIGNER–SEITZ-cell for the reciprocal lattice (introduced in the previous section) is called BRILLOUIN zone. Comparable to the site-symmetry in real space each wave vector $\mathbf{k}$ within the BRILLOUIN zone has a local symmetry.

Definition 37 (The group of the wave vector $\mathbf{k}$). *The group $\mathcal{R}(\mathbf{k})$ of the wave vector $\mathbf{k}$ is given by the subgroup of a space group $\mathcal{R}$ containing all symmetry operations $\{\underline{\mathcal{R}}(T) \mid \mathbf{t}_T + \mathbf{r}_T\}$, where the rotational part has the property*

$$\underline{\mathcal{R}}(T)\mathbf{k} = \mathbf{K}_m + \mathbf{k}. \quad (6.24)$$

In the definition $\mathbf{t}_T$ denotes a primitive lattice translation whereas $\mathbf{r}_T$ denotes a nonprimitive translation which is zero for symmorphic and nonzero for nonsymmorphic symmetry elements $T \in \mathcal{R}$ (see Section 4.2). Equation (6.24) indicates that the rotational part of a space group element T transforms the vector $\mathbf{k}$ into an equivalent wave vector $\mathbf{k}' = \mathbf{K}_m + \mathbf{k}$. Regarding the Γ point of the BRILLOUIN zone with the wave vector $\mathbf{k} = \mathbf{0}$, it follows that $\mathcal{R}(\mathbf{0})$ is given by the space group itself. Analogously, to the space group itself, the rotational part $\mathcal{G}_0(\mathbf{k})$ of each group $\mathcal{R}(\mathbf{k})$ forms a group that is not necessarily a subgroup of $\mathcal{R}(\mathbf{k})$. For every wave vector $\mathbf{k}$ at least one element can be found that transforms $\mathbf{k}$ into itself, namely the identity. So-called high symmetry points, high symmetry lines, and high symmetry planes within the BRILLOUIN zone denote specific values of $\mathbf{k}$ where $\mathcal{R}(\mathbf{k})$ is nontrivial and contains at least two elements. The group of the wave vector $\mathbf{k}$ can be computed by means of the command **GTGroupOfk**.

Since $\mathcal{R}(\mathbf{k})$ is a subgroup of $\mathcal{R}$, there are $M(\mathbf{k})$ left cosets, where $M(\mathbf{k})$ is an integer (refer to Theorem 6),

$$\mathcal{R} = T_1\mathcal{R}(\mathbf{k}) + T_2\mathcal{R}(\mathbf{k}) + \cdots + T_{M(\mathbf{k})}\mathcal{R}(\mathbf{k}). \quad (6.25)$$

Starting from an arbitrary vector $\mathbf{k}$, a representative of each coset will transform $\mathbf{k}$ into a unique copy of $\mathbf{k}$.

Definition 38 (The star of the wave vector $\mathbf{k}$). *Let $T_i = \{\underline{\mathcal{R}}(T_i) \mid \mathbf{r}_{T_i}\}$, $i = 1, \dots, M(\mathbf{k})$ be a set of coset representatives for the decomposition of $\mathcal{R}$ into $M(\mathbf{k})$ left cosets with respect to $\mathcal{R}(\mathbf{k})$. The star of $\mathbf{k}$ is defined to be the set of $M(\mathbf{k})$ vectors $\mathbf{k}_i$ obtained by*

$$\mathbf{k}_i = \underline{\mathcal{R}}(T_i)\mathbf{k}. \quad (6.26)$$

The less elements within the star of $\mathbf{k}$, the more elements are within the group $\mathcal{R}(\mathbf{k})$. Within GTPack, the star of $\mathbf{k}$ can be calculated using **GTStarOfk**.

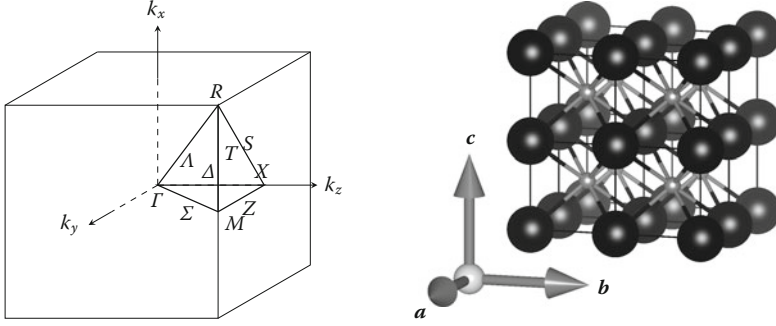


Figure 6.2 BRILLOUIN zone for the simple cubic lattice and the cesium chloride structure.

Example 37 (High symmetry points and lines of the cesium chloride lattice). As an example for the calculation of the group of the wave vector **k** and the star of **k** the cesium chloride lattice is considered (Figure 6.2). It is a simple cubic lattice (with two atoms in the elementary unit cell) and the basis vectors are given by

$$\mathbf{a}_1 = (a, 0, 0), \quad \mathbf{a}_2 = (0, a, 0), \quad \text{and} \quad \mathbf{a}_3 = (0, 0, a). \quad (6.27)$$

According to Example 36, the reciprocal basis can be calculated by means of **GTReciprocalBasis**. By choosing $a = 2\pi$, the reciprocal basis is given by

$$\mathbf{b}_1 = (1, 0, 0), \quad \mathbf{b}_2 = (0, 1, 0), \quad \text{and} \quad \mathbf{b}_3 = (0, 0, 1). \quad (6.28)$$

The BRILLOUIN zone is shown in Figure 6.2. The group of the wave vector **k** as well as the star of **k** are calculated at the points $\Gamma = (0, 0, 0)$, $M = (\frac{1}{2}, \frac{1}{2}, 0)$, and along the line $\Sigma = (\sigma, \sigma, 0)$, connecting the points Γ and M . To do so, the commands **GTGroupOfk** and **GTStarOfk** can be applied as shown in Figure 6.3. Within both commands the space group of the lattice is needed, which is given by the symmorphic space group O_h^1 in the present example. It can be installed using **GTInstallGroup**, as explained in Example 15. Furthermore, the **k** vector itself as well as the reciprocal basis needs to be specified. At the Γ point, $\mathcal{G}_0(\mathbf{k})$ is given by the whole group O_h and, therefore, the star consists of only one element, namely the $\mathbf{k} = (0, 0, 0)$ point. At M , the symmetry is reduced to $\mathcal{G}_0(\mathbf{k}) = D_{4h}$ having 16 elements. Hence, three vectors can be expected in the star of M . Along the high symmetry line Σ , $\mathcal{G}_0(\mathbf{k})$ is given by C_{2v} . Since $\text{ord}(C_{2v}) = 4$, there are 12 vectors in the star of each vector $(\sigma, \sigma, 0)$.

Example 38 (Constructing the BRILLOUIN zone in GTPack). An example for the construction of the WIGNER–SEITZ cell in real space using GTPack was given in Section 4.2.3, Example 17. Within the example, the command **GTVoronoiCell** was applied. The same strategy can be used in reciprocal space for the construction of the BRILLOUIN zone. For the example, the body-centered cubic lattice (bcc) is considered. The basis vectors are given by

$$\mathbf{a}_1 = \frac{a}{2}(1, 1, -1), \quad \mathbf{a}_2 = \frac{a}{2}(-1, 1, 1), \quad \text{and} \quad \mathbf{a}_3 = \frac{a}{2}(1, -1, 1). \quad (6.29)$$

Mathematica

GTGroupOfK, GTStarOfK

For brevity the lattice constant a is chosen to be 2π . The basis vectors of the simple cubic lattice are given by

```
In[9]:= basis = a {{1, 0, 0}, {0, 1, 0}, {0, 0, 1}} /. a -> 2  $\pi$ 
```

```
Out[9]= {{2  $\pi$ , 0, 0}, {0, 2  $\pi$ , 0}, {0, 0, 2  $\pi$ }}
```

The reciprocal basis is calculated using `GTReciprocalBasis`.

```
In[10]:= recbas = GTReciprocalBasis[basis]
```

```
Out[10]= {{1, 0, 0}, {0, 1, 0}, {0, 0, 1}}
```

The space group of the cesium chloride structure is given by O_h^1 .

```
In[11]:= grp = GTInstallGroup[Oh1];
```

The Γ -Point (0,0,0)

```
In[12]:= GTGroupOfK[grp, {0, 0, 0}, recbas]
```

$$\begin{aligned} \text{Out}[12] = & \left\{ \langle Ee, \{0, 0, 0\} \rangle, \langle C_{2z}, \{0, 0, 0\} \rangle, \langle C_{2y}, \{0, 0, 0\} \rangle, \langle C_{2xz}, \{0, 0, 0\} \rangle, \langle C_{3z}^1, \{0, 0, 0\} \rangle, \right. \\ & \langle C_{3y}^1, \{0, 0, 0\} \rangle, \langle C_{3x}^1, \{0, 0, 0\} \rangle, \langle C_{3z}^2, \{0, 0, 0\} \rangle, \langle C_{3y}^2, \{0, 0, 0\} \rangle, \\ & \langle C_{3x}^2, \{0, 0, 0\} \rangle, \langle C_{3z}^3, \{0, 0, 0\} \rangle, \langle C_{2x}, \{0, 0, 0\} \rangle, \langle C_{2y}, \{0, 0, 0\} \rangle, \langle C_{2z}, \{0, 0, 0\} \rangle, \\ & \langle C_{1z}^1, \{0, 0, 0\} \rangle, \langle C_{4x}, \{0, 0, 0\} \rangle, \langle C_{2e}, \{0, 0, 0\} \rangle, \langle C_{2\epsilon}, \{0, 0, 0\} \rangle, \langle C_{2\epsilon}^1, \{0, 0, 0\} \rangle, \\ & \langle C_{1y}^1, \{0, 0, 0\} \rangle, \langle C_{2c}, \{0, 0, 0\} \rangle, \langle C_{4y}, \{0, 0, 0\} \rangle, \langle C_{2d}, \{0, 0, 0\} \rangle, \\ & \langle IBe, \{0, 0, 0\} \rangle, \langle IC_{2x}, \{0, 0, 0\} \rangle, \langle IC_{2y}, \{0, 0, 0\} \rangle, \langle IC_{2xz}, \{0, 0, 0\} \rangle, \\ & \langle IC_{3z}^1, \{0, 0, 0\} \rangle, \langle IC_{3y}^1, \{0, 0, 0\} \rangle, \langle IC_{3x}^1, \{0, 0, 0\} \rangle, \langle IC_{3z}^2, \{0, 0, 0\} \rangle, \\ & \langle IC_{3y}^2, \{0, 0, 0\} \rangle, \langle IC_{3x}^2, \{0, 0, 0\} \rangle, \langle IC_{3z}^3, \{0, 0, 0\} \rangle, \langle IC_{2e}, \{0, 0, 0\} \rangle, \\ & \langle IC_{2x}, \{0, 0, 0\} \rangle, \langle IC_{2y}, \{0, 0, 0\} \rangle, \langle IC_{4z}, \{0, 0, 0\} \rangle, \langle IC_{2z}^1, \{0, 0, 0\} \rangle, \\ & \langle IC_{4x}, \{0, 0, 0\} \rangle, \langle IC_{2e}, \{0, 0, 0\} \rangle, \langle IC_{2\epsilon}, \{0, 0, 0\} \rangle, \langle IC_{2\epsilon}^1, \{0, 0, 0\} \rangle, \\ & \langle IC_{4y}, \{0, 0, 0\} \rangle, \langle IC_{2c}, \{0, 0, 0\} \rangle, \langle IC_{4y}, \{0, 0, 0\} \rangle, \langle IC_{2d}, \{0, 0, 0\} \rangle \} \end{aligned}$$

```
In[13]:= GTStarOfK[grp, {0, 0, 0}, recbas]
```

```
Out[13]= {{0, 0, 0}}
```

The M-Point (1/2,1/2,0)

```
In[14]:= GTGroupOfK[grp, {1 / 2, 1 / 2, 0}, recbas]
```

$$\begin{aligned} \text{Out}[14]= & \left\{ \langle \text{Ee}, \{0, 0, 0\} \rangle, \langle \text{C}_{2\text{zx}}, \{0, 0, 0\} \rangle, \langle \text{C}_{2\text{zy}}, \{0, 0, 0\} \rangle, \langle \text{C}_{2\text{xz}}, \{0, 0, 0\} \rangle, \right. \\ & \langle \text{C}_{2\text{zy}}, \{0, 0, 0\} \rangle, \langle \text{C}_{2\text{yz}}, \{0, 0, 0\} \rangle, \langle \text{C}_{4\text{yz}}, \{0, 0, 0\} \rangle, \langle \text{C}_{4\text{z}}^{\frac{1}{2}}, \{0, 0, 0\} \rangle, \\ & \langle \text{IBe}, \{0, 0, 0\} \rangle, \langle \text{IC}_{2\text{zx}}, \{0, 0, 0\} \rangle, \langle \text{IC}_{2\text{zy}}, \{0, 0, 0\} \rangle, \langle \text{IC}_{2\text{xz}}, \{0, 0, 0\} \rangle, \\ & \left. \langle \text{IC}_{2\text{zy}}, \{0, 0, 0\} \rangle, \langle \text{IC}_{2\text{yz}}, \{0, 0, 0\} \rangle, \langle \text{IC}_{4\text{yz}}, \{0, 0, 0\} \rangle, \langle \text{IC}_{4\text{z}}^{\frac{1}{2}}, \{0, 0, 0\} \rangle \right\} \end{aligned}$$

```
In[15]:= GTStarOfK[grp, {1 / 2, 1 / 2, 0}, recbas]
```

$$\text{Out}[15]=\left\{\left\{-\frac{1}{2}, -\frac{1}{2}, 0\right\}, \left\{-\frac{1}{2}, 0, -\frac{1}{2}\right\}, \left\{0, -\frac{1}{2}, -\frac{1}{2}\right\}\right\}$$

The Σ -Axis $(\sigma, \sigma, 0)$

```
In[16]:= GTGroupOfK[grp, {σ, σ, 0}, recbas]
```

$$\text{Out}[16]=\left\{\langle \text{Ee}, \{0, 0, 0\} \rangle, \langle \text{C}_{2a}, \{0, 0, 0\} \rangle, \langle \text{IC}_{2z}, \{0, 0, 0\} \rangle, \langle \text{IC}_{2b}, \{0, 0, 0\} \rangle\right\}$$

```
In[17]:= GTStarOfK[grp, {σ, σ, 0}, recbas]
```

```
Out[17]= {{0, -σ, -σ}, {0, -σ, σ}, {0, σ, -σ}, {0, σ, σ}, {-σ, 0, -σ}, {-σ, 0, σ},
          {-σ, -σ, 0}, {-σ, σ, 0}, {σ, 0, -σ}, {σ, 0, σ}, {σ, -σ, 0}, {σ, σ, 0}}
```

Figure 6.3 Calculation of the group of the wave vector $\mathbf{k}$ as well as the star of $\mathbf{k}$ for the high symmetry points Γ and M and the high symmetry line Σ for the cesium chloride lattice.

Mathematica**GTVoronoiCell, GTBZPath**

The high-symmetry points for the face centered cubic lattice can be obtained using GTBZPath.

```
In[9]:= kpath = GTBZPath["bcc"]
```

```
Out[9]:= {{0, 0, 0}, {0, 0, 1}, {0, 1/2, 1/2}, {0, 0, 0}, {1/2, 1/2, 1/2}, {0, 1/2, 1/2}, {Γ, H, N, Γ, P, N}}
```

The reciprocal basis is calculated with the help of GTReciprocalBasis.

```
In[10]:= basis = a/2 {{1, 1, -1}, {-1, 1, 1}, {1, -1, 1}} /. a -> 2 π;
recbas = GTReciprocalBasis[basis];
```

Using GTVoronoiCell, the Brillouin zone can be constructed. The high-symmetry points can be included into the plot.

```
In[12]:= GTVoronoiCell[recbas, {8, 2, 4}, kpath]
```

```
■ x-axis ■ y-axis ■ z-axis
```

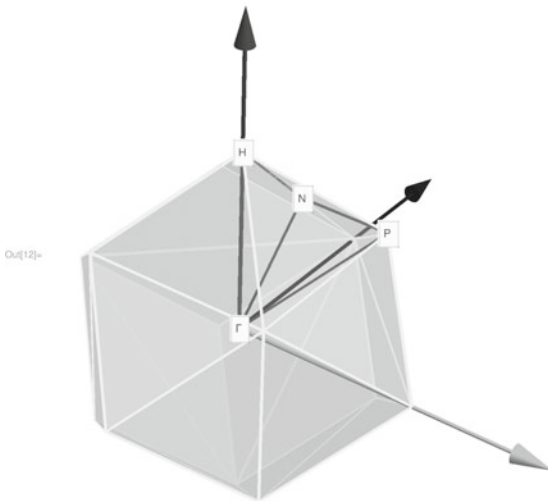


Figure 6.4 Construction of the BRILLOUIN zone for the body-centered cubic lattice using GTVoronoiCell. The information about high symmetry points are obtained using GTBZPath.

and the lattice constant is set to $a = 2\pi$. In addition to the BRILLOUIN zone the high symmetry points of the bcc lattice are incorporated into the plot. These are obtained by applying the command **GTBZPath**. An example notebook is shown in Figure 6.4.

Task 23 (Brillouin zone of fcc). Follow Example 38 and construct the BRILLOUIN zone for an fcc lattice. Additionally, use **GTBravaisLattice** to construct other 3-dimensional lattices and repeat the scheme to plot the associated BRILLOUIN zones.

6.4

Irreducible Representations of Symmorphic Space Groups

The concept of a space group was introduced in Section 4.2.2, as the group of all transformations that leave a crystal invariant. Among all possible space groups, the symmorphic space groups represent a special class where the translational part of each space group element T is given by a primitive translation of the lattice $\mathbf{t}_T$. Symmorphic space groups have the special structure

$$\mathcal{R} = \mathcal{T} \rtimes \mathcal{G}_0 . \quad (6.30)$$

That means, $\mathcal{R}$ can be written as a semidirect product of the group of pure translations $\mathcal{T}$ and the group of all rotational parts of the space group elements $\mathcal{G}_0$, where $\mathcal{T}$ is an invariant Abelian subgroup of $\mathcal{R}$. Hence, it is possible to apply the theory of induced representations presented in Section 5.7 to calculate all irreducible representations of a symmorphic space group. To do so, it is necessary to estimate the needed quantities mentioned in equation (5.152).

The irreducible representations of the translation group $\mathcal{T}$ were discussed in connection with BLOCH's ansatz in Section 6.1. Since $\mathcal{T}$ is Abelian, all representations are one-dimensional. They are indexed by the reciprocal vector $\mathbf{k}$ and the representation matrices are equal to the characters $\chi^{\mathbf{k}}$,

$$\chi^{\mathbf{k}}(\mathbf{t}) = e^{-i\mathbf{k} \cdot \mathbf{t}} , \quad \text{for all } \mathbf{t} \in \mathcal{T} . \quad (6.31)$$

These characters are defined up to reciprocal lattice vectors $\mathbf{K}_m$ with the property

$$e^{-i\mathbf{t} \cdot \mathbf{K}_n} = 1 , \quad (6.32)$$

as introduced in Section 6.2, equation (6.18). Therefore, with respect to equation (5.125), all elements $B \in \mathcal{G}_0$ with the property

$$\chi^{\mathbf{k}}(\{\underline{\mathbf{R}}(T) \mid \mathbf{0}\} \{\underline{\mathbf{1}} \mid \mathbf{t}\} \{\underline{\mathbf{R}}(T) \mid \mathbf{0}\}^{-1}) = \chi^{\mathbf{k}}(\{\underline{\mathbf{1}} \mid \mathbf{t}\}) \quad (6.33)$$

have to fulfill the equation

$$\underline{\mathbf{R}}(T)\mathbf{k} = \mathbf{K}_n + \mathbf{k} , \quad (6.34)$$

where $\mathbf{K}_n$ denotes a reciprocal lattice vector. That means, the little group $\mathcal{G}_0(\mathbf{k})$ (Definition 33) is given by all rotational parts of the group of the wave vector $\mathcal{R}(\mathbf{k})$ (Definition 37) and the orbit (Definition 34) is related to the star of $\mathbf{k}$ (Definition 38). The group of the wave vector $\mathbf{k}$ itself represents the group $\mathcal{S}(q)$ in equation (5.141).

According to Theorem 31 the decomposition of the symmorphic space group $\mathcal{R}$ into right cosets with respect to $\mathcal{R}(\mathbf{k})$ is equal to the decomposition of the point group of the lattice $\mathcal{G}_0$ into right cosets with respect to $\mathcal{G}_0(\mathbf{k})$. Let the rotations $\underline{\mathbf{R}}_1, \underline{\mathbf{R}}_2, \dots, \underline{\mathbf{R}}_{M(\mathbf{k})} \in \mathcal{G}_0$ denote the $M(\mathbf{k})$ coset representatives,

$$\mathcal{G}_0 = \mathcal{G}_0(\mathbf{k})\underline{\mathbf{R}}_1 + \mathcal{G}_0(\mathbf{k})\underline{\mathbf{R}}_2 + \dots + \mathcal{G}_0(\mathbf{k})\underline{\mathbf{R}}_{M(\mathbf{k})} . \quad (6.35)$$

Then, according to Theorem 32 all irreducible representations $\Gamma^{\mathbf{k},p}$ of $\mathcal{R}$ can be indexed by the combined index $(\mathbf{k}, p)$, where p denotes an index over the irreducible representations $\Gamma_{\mathcal{G}_0(\mathbf{k})}^p$ of the point group $\mathcal{G}_0(\mathbf{k})$. The representation matrices of an element $\{\underline{\mathbf{R}} \mid \mathbf{t}\} \in \mathcal{R}$ are given by

$$\Gamma^{\mathbf{k},p}(\{\underline{\mathbf{R}} \mid \mathbf{t}\})_{kt,jr} = \begin{cases} e^{-i(\underline{\mathbf{R}}_k \mathbf{t}) \cdot \mathbf{t}} \Gamma_{\mathcal{G}_0(\mathbf{k})}^p \left(\underline{\mathbf{R}}_k \underline{\mathbf{R}}_j^{-1} \right)_{tr}, & \text{if } \underline{\mathbf{R}}_k \underline{\mathbf{R}}_j^{-1} \in \mathcal{G}_0(\mathbf{k}) \\ 0, & \text{if } \underline{\mathbf{R}}_k \underline{\mathbf{R}}_j^{-1} \notin \mathcal{G}_0(\mathbf{k}) \end{cases} . \quad (6.36)$$

Consequently, the characters of the representations can be calculated according to

$$\chi^{\mathbf{k},p}(\{\underline{\mathbf{R}} \mid \mathbf{t}\}) = \sum_{\langle j \rangle} e^{-i(\underline{\mathbf{R}}_k \mathbf{t}) \cdot \mathbf{t}} \chi_{\mathcal{G}_0(\mathbf{k})}^p \left(\underline{\mathbf{R}}_j \underline{\mathbf{R}}_j^{-1} \right) , \quad (6.37)$$

where $\langle j \rangle$ denotes the sum over all coset representatives with the property $\underline{\mathbf{R}}_j \underline{\mathbf{R}}_j^{-1} \in \mathcal{G}_0(\mathbf{k})$. From the theory of induced representations it follows that finding all irreducible representations of an infinite group can be reduced to calculating the irreducible representations of a finite and rather small point group.

Within GTPack, the calculation of character tables for space groups is implemented within the command **GTCharacterTableOfk**. However, since the application of the command is independent of a space group being symmorphic or not, an example is postponed to the end of the next section.

6.5

Irreducible Representations of Nonsymmorphic Space Groups

Even though the group $\mathcal{T}$ of all primitive translations that leave the crystal invariant is still an Abelian invariant subgroup, a nonsymmorphic space group can not be expressed as a semidirect product of a pure point group and $\mathcal{T}$ as for the symmorphic space groups. Nevertheless, the irreducible representations of a nonsymmorphic space group $\mathcal{R}$ can be calculated by induction. In general, space groups (symmorphic and nonsymmorphic) are solvable, i.e., it is possible to construct a composition series in terms of invariant subgroups $\mathcal{H}_i$,

$$\mathcal{T} \triangleleft \mathcal{H}_1 \triangleleft \mathcal{H}_2 \triangleleft \cdots \triangleleft \mathcal{H}_n = \mathcal{R} , \quad (6.38)$$

such that all factor groups $\mathcal{H}_i/\mathcal{H}_{i+1}$ are cyclic groups of index 2 or 3 [98, 99]. The irreducible representations of nonsymmorphic space groups can be induced following the composition series, starting from a symmorphic space group $\mathcal{H}_i^{(3)}$.

- 3) Here, it will be shown how irreducible representations of space groups can be obtained and how the theory is embedded into GTPack. For a more rigorous discussion see [36, 100].

If $\mathcal{H}$ is an invariant subgroup of $\mathcal{R}$ of index 2 (i.e., $\text{ord}(\mathcal{R})/\text{ord}(\mathcal{H}) = 2$), then $\mathcal{R}$ can be written as

$$\mathcal{R} = \mathcal{H} + \mathcal{H}q. \quad (6.39)$$

Analogously, if $\mathcal{H}$ has index 3, $\mathcal{R}$ can be written as

$$\mathcal{R} = \mathcal{H} + \mathcal{H}q + \mathcal{H}q^2. \quad (6.40)$$

The elements $q, q^2 \in \mathcal{R}$ are coset representatives of the decomposition of $\mathcal{R}$ into right cosets with respect to $\mathcal{H}$. For an irreducible representation $\Gamma_{\mathcal{H}}^p$ of $\mathcal{H}$ it is possible to define the conjugate representation $(\Gamma_{\mathcal{H}}^p)_g$, given by

$$(\underline{\Gamma}_{\mathcal{H}}^p(h))_g = \underline{\Gamma}_{\mathcal{H}}^p(g^{-1}hg), \quad g \in \mathcal{R}, \quad h \in \mathcal{H}. \quad (6.41)$$

There are two cases to distinguish. Either $(\Gamma_{\mathcal{H}}^p)_g$ is equivalent to $\Gamma_{\mathcal{H}}^p$ or it is inequivalent to $\Gamma_{\mathcal{H}}^p$. Analogously to Definition 33, the little group is given by all elements $g \in \mathcal{R}$ with the property $(\Gamma_{\mathcal{H}}^p)_g \sim \Gamma_{\mathcal{H}}^p$. The set of the inequivalent representations $(\Gamma_{\mathcal{H}}^p)_g$ forms the orbit of $\Gamma_{\mathcal{H}}^p$. In the special case of $\mathcal{H}$ being an invariant subgroup of index 2 or 3, the little group of $\Gamma_{\mathcal{H}}^p$ is either the whole group $\mathcal{R}$ (length of the orbit is 1) or the group $\mathcal{H}$ (length of the orbit is 2 or 3).

Starting with the second case (the length of the orbit is 2 or 3) then according to Theorem 28, equation (5.117) the matrices of the induced representation Γ^p of $\mathcal{R}$ can be obtained via

$$\underline{\Gamma}^p(h) = \begin{pmatrix} \underline{\Gamma}_{\mathcal{H}}(h) & 0 \\ 0 & (\underline{\Gamma}_{\mathcal{H}}(h))_q \end{pmatrix}, \quad (6.42)$$

for every $h \in \mathcal{H} \subset \mathcal{R}$ and

$$\underline{\Gamma}^p(q) = \begin{pmatrix} 0 & \underline{\Gamma}_{\mathcal{H}}(q^2) \\ \underline{1} & 0 \end{pmatrix}, \quad (6.43)$$

for the coset representative $q \in \mathcal{R}$. All other elements $T = qh$ with $h \in \mathcal{H}$ can be obtained from the matrices above. Similarly for index 3 it is possible to write

$$\underline{\Gamma}^p(h) = \begin{pmatrix} \underline{\Gamma}_{\mathcal{H}}(h) & 0 & 0 \\ 0 & (\underline{\Gamma}_{\mathcal{H}}(h))_q & 0 \\ 0 & 0 & (\underline{\Gamma}_{\mathcal{H}}(h))_{q^2} \end{pmatrix}, \quad (6.44)$$

and

$$\underline{\Gamma}^p(q) = \begin{pmatrix} 0 & 0 & \underline{\Gamma}_{\mathcal{H}}(q^3) \\ \underline{1} & 0 & 0 \\ 0 & \underline{1} & 0 \end{pmatrix}. \quad (6.45)$$

In the case where the little group of an irreducible representation of $\mathcal{H}$ is the whole group $\mathcal{R}$ (the length of the orbit is 1) it is possible to construct 2 irreducible representations of $\mathcal{R}$ from $\Gamma_{\mathcal{H}}^p$ in the case of index 2 and 3 irreducible representations of $\mathcal{R}$ from $\Gamma_{\mathcal{H}}^p$ in the case of index 3. The matrices are given by

$$\underline{\underline{\Gamma}}^{p,1}(h) = \underline{\underline{\Gamma}}^{p,2}(h) = \underline{\underline{\Gamma}}_{\mathcal{H}}(h), \quad (6.46)$$

for $h \in \mathcal{H}$ and

$$\underline{\underline{\Gamma}}^{p,1}(q) = -\underline{\underline{\Gamma}}^{p,2}(q) = \underline{\underline{U}}. \quad (6.47)$$

The matrix $\underline{\underline{U}}$ has to be determined by

$$(\underline{\underline{\Gamma}}_{\mathcal{H}}(h))_q = \underline{\underline{U}}^{-1} \underline{\underline{\Gamma}}_{\mathcal{H}}(h) \underline{\underline{U}} \quad (6.48)$$

and

$$\underline{\underline{U}}^2 = \underline{\underline{\Gamma}}_{\mathcal{H}}(h^2). \quad (6.49)$$

Similarly in the case of index 3 one obtains

$$\underline{\underline{\Gamma}}^{p,1}(h) = \underline{\underline{\Gamma}}^{p,2}(h) = \underline{\underline{\Gamma}}^{p,3}(h) = \underline{\underline{\Gamma}}_{\mathcal{H}}(h), \quad (6.50)$$

for $h \in \mathcal{H}$ and

$$\underline{\underline{\Gamma}}^{p,1}(q) = \epsilon \underline{\underline{\Gamma}}^{p,2}(q) = \epsilon^2 \underline{\underline{\Gamma}}^{p,3}(q) = \underline{\underline{U}}, \quad \text{with } \epsilon = e^{\frac{2\pi}{3}i}. \quad (6.51)$$

Here, $\underline{\underline{U}}$ has to fulfill the conditions

$$(\underline{\underline{\Gamma}}_{\mathcal{H}}(h))_q = \underline{\underline{U}}^{-1} \underline{\underline{\Gamma}}_{\mathcal{H}}(h) \underline{\underline{U}} \quad (6.52)$$

and

$$\underline{\underline{U}}^2 = \underline{\underline{\Gamma}}_{\mathcal{H}}(h^2). \quad (6.53)$$

More than 100 nonsymmorphic space groups contain an invariant subgroup of index 2. Only the four groups C_3^2 , C_3^3 , C_6^4 , and C_6^5 contain subgroups of index 3 [98]. The induction method described above can be applied when an invariant subgroup of index 2 or 3 can be found that is a symmorphic group. Representation matrices of symmorphic space groups can be obtained in a straightforward way as explained in the previous section. In case a nonsymmorphic space group has no invariant symmorphic subgroup of index 2 or 3 the procedure has to be repeated once more until a symmorphic subgroup of index 2 or 3 can be found.

As in the case of symmorphic space groups one starts with the construction of irreducible representations $\Gamma_{\mathcal{R}(\mathbf{k})}^p$ of the group $\mathcal{R}(\mathbf{k}) \subset \mathcal{R}$, the group of the wave vector $\mathbf{k}$. However, not every representation is valid for the construction of irreducible representations of the whole space group.

Definition 39 (Allowed representation). Let $\Gamma_{\mathcal{R}(\mathbf{k})}^p$ be a unitary irreducible representation of $\mathcal{R}(\mathbf{k})$, the group of the wave vector $\mathbf{k}$. $\Gamma_{\mathcal{R}(\mathbf{k})}^p$ is called an allowed representation if

$$\underline{\Gamma}_{\mathcal{R}(\mathbf{k})}^p(\{\underline{\mathbf{1}} \mid \mathbf{t}\}) = e^{i\mathbf{k} \cdot \mathbf{t}} \underline{\Gamma}_{\mathcal{R}(\mathbf{k})}^p(\{\underline{\mathbf{1}} \mid \mathbf{0}\}), \quad \text{for every } \mathbf{t} \in \mathcal{T}. \quad (6.54)$$

The representation matrices of each element $T = \{\underline{\mathbf{R}}(T) \mid \mathbf{r}_T + \mathbf{t}_T\}$ of the space group $\mathcal{R}$ can be calculated from the allowed representations $\Gamma_{\mathcal{R}(\mathbf{k})}^p$ of the group $\mathcal{R}(\mathbf{k})$ via

$$\Gamma^{\mathbf{k},p}(\{\underline{\mathbf{R}}(T) \mid \mathbf{r}_T + \mathbf{t}_T\})_{kt,jr} = \begin{cases} e^{-i(\underline{\mathbf{R}}(T)\mathbf{k}) \cdot \mathbf{t}_T} \Gamma_{\mathcal{R}(\mathbf{k})}^p(T_k T T_j^{-1})_{tr}, & \text{if } T_k T T_j^{-1} \in \mathcal{R}(\mathbf{k}) \\ 0, & \text{if } T_k T T_j^{-1} \notin \mathcal{R}(\mathbf{k}) \end{cases}. \quad (6.55)$$

It follows that the characters of the representations can be calculated according to

$$\chi^{\mathbf{k},p}(\{\underline{\mathbf{R}}(T) \mid \mathbf{r}_T + \mathbf{t}_T\}) = \sum_{\langle j \rangle} e^{-i(\underline{\mathbf{R}}(T)\mathbf{k}) \cdot \mathbf{t}_T} \chi_{\mathcal{R}(\mathbf{k})}^p(T_j T T_j^{-1}). \quad (6.56)$$

Again, $\langle j \rangle$ denotes that the sum is over all coset representatives with the property $T_j T T_j^{-1} \in \mathcal{R}(\mathbf{k})$.

Example 39 (Calculating the character table for space groups). As an example the character table of the space group $P2_1/c$ (#14) will be calculated by applying the command **GTCharacterTableOfK** (Figure 6.5). The command uses the algorithm of Zak [98]. The group $P2_1/c$ has the following coset representatives

$$T_1 = \{E \mid (0, 0, 0)\} \quad (6.57)$$

$$T_2 = \{I \mid (0, 0, 0)\}, \quad (6.58)$$

$$T_3 = \{C_{2y} \mid (0, 1/2, 1/2)\}, \quad (6.59)$$

$$T_4 = \{IC_{2y} \mid (0, 1/2, 1/2)\}. \quad (6.60)$$

It can be installed by using **GTInstallGroup** as shown in Figure 6.5. $P2_1/c$ is a monoclinic space group. The basis vectors of the monoclinic lattice are obtained from **GTBravaisLattice** and given by

$$a_1 = (a, 0, 0) \quad (6.61)$$

$$a_2 = (0, b, 0), \quad (6.62)$$

$$a_3 = (c \cos(\beta), 0, c \sin(\beta)). \quad (6.63)$$

The associated reciprocal basis vectors are calculated using **GTReciprocalBasis**. The character table itself is calculated for the Γ point $\mathbf{k} = (0, 0, 0)$ and the Y point $\mathbf{k} = (1/2, 0, 0)$ at the Brillouin zone boundary (vectors specified in units of reciprocal basis vectors). At the Γ point, the character table is similar to the character

Mathematica**GTCharacterTableOfK**

The basis vectors of the primitive monoclinic lattice are obtained via GTBravaisLattice. GTReciprocalBasis is used to calculate the reciprocal basis vectors.

```
In[9]:= basis = GTBravaisLattice[{"Monoclinic", "P"}]
      repbas = GTReciprocalBasis[basis];
```

```
Out[9]:= {{a, 0, 0}, {0, b, 0}, {c Cos[β], 0, c √(1 - Cos[β]^2)}}
```

The character table will be calculated for the space group $P2_1/c$ with the space group number 14.

```
In[11]:= grp = GTInstallGroup[14]
```

```
Out[11]:= {⟨Ee, {0, 0, 0}⟩, ⟨C2y, {0, 1/2, 1/2}⟩, ⟨IC2y, {0, 1/2, 1/2}⟩, ⟨IEe, {0, 0, 0}⟩}
```

The Γ -Point (0,0,0)

```
In[12]:= kpoint = {0, 0, 0};
```

```
In[13]:= {classes, charsfinal, names} =
      GTCharacterTableOfK[grp, kpoint, repbas, GOLattice → "Fractional"];
```

	$\langle Ee, \{0, 0, 0\} \rangle$	$\langle C_{2y}, \{0, \frac{1}{2}, \frac{1}{2}\} \rangle$	$\langle IC_{2y}, \{0, \frac{1}{2}, \frac{1}{2}\} \rangle$	$\langle IEe, \{0, 0, 0\} \rangle$
Γ^1	1	1	-1	-1
Γ^2	1	-1	1	-1
Γ^3	1	1	1	1
Γ^4	1	-1	-1	1

The Y -Point (0,1/2,0)

```
In[14]:= kpoint = {0, 1/2, 0};
```

```
In[15]:= {classes, charsfinal, names} =
      GTCharacterTableOfK[grp, kpoint, repbas, GOLattice → "Fractional"];
```

	$\langle Ee, \{0, 0, 0\} \rangle$	$\langle C_{2y}, \{0, \frac{1}{2}, \frac{1}{2}\} \rangle$	$\langle IC_{2y}, \{0, \frac{1}{2}, \frac{1}{2}\} \rangle$	$\langle IEe, \{0, 0, 0\} \rangle$
Γ^1	2	0	0	0

Figure 6.5 Calculation of the character table of the monoclinic space group $P2_1/c$ (#14) at the Γ and Y point using GTCharacterTableOfK.

table of C_{2h} , containing four 1-dimensional irreducible representations. At the Y point only one irreducible representation can be found, which is 2-dimensional. Higher dimensional irreducible representations at the Brillouin zone boundary are a special property of nonsymmorphic space groups. They lead to degenerate energy levels on the Brillouin zone boundary within band structure calculations. Recently, such degeneracies have been widely discussed with respect to semimetals and Dirac nodes [25, 101–103].

Part Two

Applications in Electronic Structure Theory

7

Solution of the SCHRÖDINGER Equation

Where did we get that from? Nowhere. It's not possible to derive it from anything you know. It came out of the mind of Schrödinger...

Richard Feynman
(*The Feynman Lectures of Physics*, Vol 3: *Quantum Mechanics*,
Addison-Wesley, 1979)

This chapter deals with the application of group theory to the solution of the SCHRÖDINGER equation. The SCHRÖDINGER equation is a partial differential equation with second-order derivatives in space and a first-order derivative in time and represents the central equation of non-relativistic quantum mechanics. The SCHRÖDINGER equation contains the HAMILTON operator whose eigenvalues represent the energy levels of the system. The symmetry of the HAMILTON operator leads to the group of the SCHRÖDINGER equation. The irreducible representations of this group fully determine the symmetry of the solutions of the SCHRÖDINGER equation as well as the degeneracy of the energy levels. Furthermore, the concept of perturbation theory is introduced. Crystal field theory is a semi-empirical theory build in the framework of linear time-independent perturbation theory. Group theory is used to determine the splitting of energy levels due to a crystal field as well as the terms within the effective crystal field Hamiltonian. Finally, time-dependent perturbation theory is discussed and transition probabilities and selection rules are formulated.

7.1

The SCHRÖDINGER Equation

The central equation of nonrelativistic quantum mechanics is the SCHRÖDINGER equation,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}, t) \right] \Phi(\mathbf{r}, t) = i\hbar \frac{\partial}{\partial t} \Phi(\mathbf{r}, t). \quad (7.1)$$

It is a partial differential equation with second-order derivatives in space and a first-order derivative in time. The operator

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}, t) \quad (7.2)$$

is called the HAMILTON operator,

$$\hat{T} = -\frac{\hbar^2}{2m}\nabla^2 \quad (7.3)$$

is the operator of the kinetic energy and $U(\mathbf{r}, t)$ is the external potential which is time- and space-dependent in general. Equation (7.1) is valid for one-electron systems. For many-electron systems, it is possible to map the interacting many-particle system to an effective noninteracting one-particle system as is done in the framework of density functional theory [105, 106].

The solution of the SCHRÖDINGER equation $\Phi(\mathbf{r}, t)$ is called the *wave function*. Within the statistical interpretation, the square of the absolute value of the wave function is called the probability density function ρ ,

$$\rho(\mathbf{r}, t) = |\Phi(\mathbf{r}, t)|^2 . \quad (7.4)$$

The probability p of measuring a particle within a volume $d^3\mathbf{r}$ at the position $\mathbf{r}$ and time t is given by

$$p(\mathbf{r}, t) = d^3\mathbf{r} \rho(\mathbf{r}, t) \quad (7.5)$$

To allow for a proper normalization of the probability density function it is postulated that only those solutions are of physical meaning that are square-integrable functions ($\Phi(\mathbf{r}, t) \in L^2$).

For a time-independent external potential, e.g., as present in atomic systems

$$U(\mathbf{r}, t) = V(\mathbf{r}) , \quad (7.6)$$

the wave function can be separated into a time-dependent and a time-independent part

$$\Phi(\mathbf{r}, t) = \phi(\mathbf{r})e^{-iEt/\hbar} . \quad (7.7)$$

The differential equation for the real-space part $\phi(\mathbf{r})$ is the so-called stationary SCHRÖDINGER equation,

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \right] \phi(\mathbf{r}) = E\phi(\mathbf{r}) . \quad (7.8)$$

The separation constant E appearing in (7.7) and (7.8) is the energy of the system. The stationary SCHRÖDINGER equation (7.8) has the form of a linear eigenvalue problem.

7.2

The Group of the SCHRÖDINGER Equation

The symmetry of the Hamiltonian is determined by the symmetry of the potential $V(\mathbf{r})$ and with that by the symmetry of the system under consideration. As an illustration, examples of symmetry groups for specific molecules and atomic clusters can be found in Figure 7.1.

Following the transformation behavior of scalar functions introduced in Section 2.2.1 the transformations of the HAMILTON operator will be discussed. In general, acting with the HAMILTON operator on an arbitrary function $g(\mathbf{r})$, which is not necessarily an eigenfunction, gives another function called $f(\mathbf{r})$ in the fol-

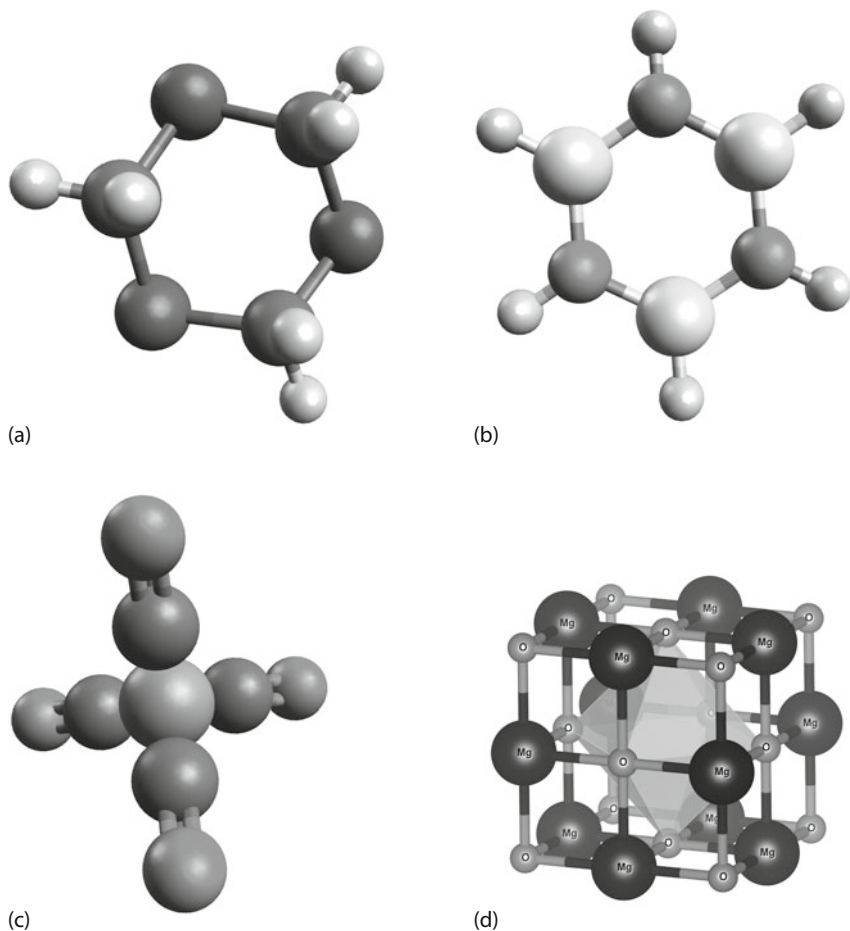


Figure 7.1 Local symmetry groups of certain molecules and atomic clusters [107, 108]. (a) 1,3,5-Trithiane, $(\text{CH}_2\text{S})_3$, C_{3v} ; (b) borazine, $\text{B}_3\text{N}_3\text{H}_6$, D_{3h} ; (c) nickel tetracarbonyl, $\text{Ni}(\text{CO})_4$, T_d ; (d) magnesium vacancy in a magnesium oxide crystal, O_h .

lowing,

$$f(\mathbf{r}) = \hat{H}(\mathbf{r})g(\mathbf{r}) . \quad (7.9)$$

A coordinate transformation T with

$$\mathbf{r}' = \underline{\underline{R}}^{-1}(T)\mathbf{r} , \quad (7.10)$$

does not change the form of (7.9),

$$f(\mathbf{r}') = \hat{H}(\mathbf{r}')g(\mathbf{r}') . \quad (7.11)$$

Applying the transformation operator $\hat{P}(T)$ to both sides of (7.9) gives

$$\hat{P}(T)f(\mathbf{r}) = \hat{P}(T)\hat{H}(\mathbf{r})g(\mathbf{r}) = \hat{P}(T)\hat{H}(\mathbf{r})\hat{P}^{-1}(T)\hat{P}(T)g(\mathbf{r}) , \quad (7.12)$$

and

$$f(\underline{\underline{R}}^{-1}(T) \cdot \mathbf{r}) = \hat{P}(T)\hat{H}(\mathbf{r})\hat{P}^{-1}(T)g(\underline{\underline{R}}^{-1}(T) \cdot \mathbf{r}) . \quad (7.13)$$

Hence, by comparing equations (7.11) and (7.13) the transformation behavior of the HAMILTON operator can be verified,

$$\hat{H}(\underline{\underline{R}}^{-1}(T) \cdot \mathbf{r}) = \hat{P}(T)\hat{H}(\mathbf{r})\hat{P}^{-1}(T) . \quad (7.14)$$

From all possible transformations T , it is possible to concentrate on those leaving the HAMILTON operator invariant,

$$\hat{H}(\mathbf{r}) = \hat{P}(T)\hat{H}(\mathbf{r})\hat{P}^{-1}(T) \quad \text{or} \quad [\hat{H}, \hat{P}] = 0 . \quad (7.15)$$

These transformations form a group that is called *the group of the SCHRÖDINGER equation*.

Definition 40 (The group of the SCHRÖDINGER equation). *The group $\mathcal{G}_{\text{SEQ}}$ of all transformations T that leave the HAMILTON operator invariant is called the group of the SCHRÖDINGER equation.*

Task 24 (Group of the SCHRÖDINGER equation). Verify that all transformations $\hat{P}(T)$ that leave the HAMILTON operator invariant form a group.

7.3

Degeneracy of Energy States

Degeneracy of energy states	
GTAngularMomentumChars	Calculates the characters of an irreducible representation of $O(3)$ for the classes of a point group
GTCrystalFieldSplitting	Calculates the decomposition of irreducible representations of a group $\mathcal{G}$ into irreducible representations of a subgroup $\mathcal{G}'$

According to Section 7.1, the SCHRÖDINGER equation is an eigenvalue equation when stationary potentials are considered,

$$\hat{H}\phi(\mathbf{r}) = E\phi(\mathbf{r}) . \quad (7.16)$$

Because of its symmetry, the Hamiltonian $\hat{H}$ is invariant under transformations contained within the group of the SCHRÖDINGER equation $\mathcal{G}_{\text{SEQ}}$. Since $\hat{H}$ is invariant under every element of $\mathcal{G}_{\text{SEQ}}$ it is an irreducible tensor operator of the identity representation of $\mathcal{G}_{\text{SEQ}}$ (see Section 5.6). To approach the solution of (7.16) ϕ is expanded in terms of basis functions $\phi_m^{p,\alpha}$ of the l_p -dimensional irreducible representations Γ^p of $\mathcal{G}_{\text{SEQ}}$

$$\phi(\mathbf{r}) = \sum_{\alpha} \sum_p \sum_{m=1}^{d_p} \phi_m^{p,\alpha}(\mathbf{r}) . \quad (7.17)$$

The index α distinguishes between different linearly independent basis functions transforming as Γ^p . Note, (7.17) does not represent an expansion with respect to a fixed basis set. The basis functions $\phi_m^{p,\alpha}(\mathbf{r})$ depend on $\phi(\mathbf{r})$. Making use of the series expansion (7.17) in (7.16) leads to the following characteristic equation for the eigenvalues,

$$\det \left[\left(\phi_n^{q,\beta}, \hat{H} \phi_m^{p,\alpha} \right) - E \delta_{pq} \delta_{mn} \delta_{\alpha\beta} \right] = 0 . \quad (7.18)$$

Equation (7.18) can be simplified by applying the WIGNER–ECKART Theorem, i.e., Theorem 27. The CLEBSCH–GORDAN coefficients involving the identity representation are given by

$$\left(\begin{matrix} p & 1 \\ m & 1 \end{matrix} \middle| \begin{matrix} q & 1 \\ n \end{matrix} \right)^* = \delta_{pq} \delta_{mn} . \quad (7.19)$$

Hence, equation (7.18) becomes block-diagonal involving the matrices

$$D(p, m)_{\beta\alpha} = \left(\phi_m^{p,\beta}, \hat{H} \phi_m^{p,\alpha} \right) - E \delta_{pq} \delta_{mn} \delta_{\alpha\beta} . \quad (7.20)$$

The eigenvalues are determined by the product of the determinants of $\underline{\underline{D}}(p, m)$ as

$$\prod_p \prod_{m=1}^{d_p} \det \underline{\underline{D}}(p, m) = 0 . \quad (7.21)$$

Furthermore, since the basis functions are defined up to a similarity transformation it follows

$$\underline{\underline{D}}(p, 1) = \underline{\underline{D}}(p, 2) = \cdots = \underline{\underline{D}}(p, d_p) . \quad (7.22)$$

Consequently, each electronic state associated with a l_p -dimensional irreducible representation Γ^p exhibits at least a l_p -fold degeneracy. The result is summarized in the so-called matrix element theorem.

Theorem 35 (Matrix-element theorem). *Let Γ^p and Γ^q be two l_p - and l_q -dimensional irreducible representations of the group of the SCHRÖDINGER equation G_{SEQ} . Γ^p and Γ^q are not equivalent if $p \neq q$. For $p = q$ the representations are identical. The associated basis functions are $\phi_1^p, \dots, \phi_{l_p}^p$ and $\phi_1^q, \dots, \phi_{l_q}^q$. Then, the matrix elements of the HAMILTON operator are given by*

$$\int_{\mathbb{R}^3} d^3\mathbf{r} \phi_m^p(\mathbf{r})^* \hat{H} \phi_n^q(\mathbf{r}) = \delta_{p,q} \delta_{m,n} E^p. \quad (7.23)$$

If $p = q$ and $m = n$ the matrix element is independent of m .

Example 40 (Splitting of energy levels in crystal fields). The degeneracy of an energy eigenvalue of the SCHRÖDINGER equation is equal to the dimension of the associated irreducible representation. That means, as soon as the symmetry is decreased to a subgroup of the original group of the SCHRÖDINGER equation, the irreducible representation becomes reducible in general, which results in a splitting of the energy level. A prominent example is the splitting of d -states in an octahedral crystal field as is present e.g., for the perovskites BaTiO_3 or SrTiO_3 . For a single atom, the 5-fold degenerate d -states belong to the irreducible representation D^2 of the rotational group $O(3)$. However, D^2 is reducible for octahedral symmetry, which the point group O_h belongs to.

With the help of **GTAngularMomentumChars** the characters of D^2 can be calculated for the classes of O_h . Afterwards, the decomposition of D^2 into irreducible representations of O_h can be estimated by applying **GTirep**. As can be verified from Figure 7.2, D^2 splits into the representations T_{2g} and E_g ,

$$D^2 \simeq T_{2g} \oplus E_g. \quad (7.24)$$

By applying uniaxial strain in the crystallographic c -direction, the octahedral symmetry is decreased, as can be seen in Figure 7.2¹⁾. The new symmetry group

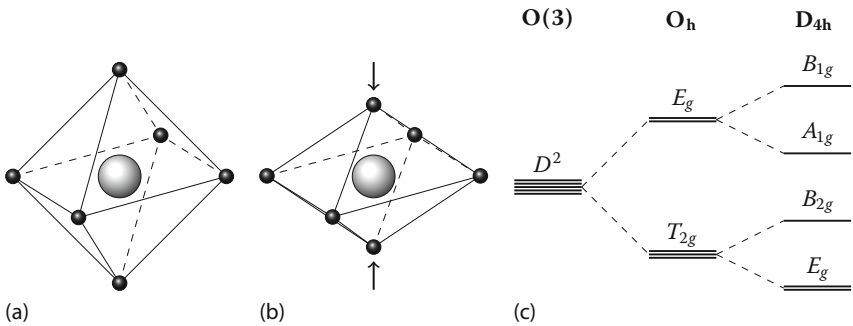


Figure 7.2 Splitting of d -states in a crystal field. (a) Octahedral crystal field with O_h symmetry. (b) Uniaxial strain reduces symmetry to D_{4h} . (c) Splitting of d -states within the crystal field.

- 1) Even though it is possible to determine which irreducible representations occur within a crystal field splitting, it is not possible to estimate the ordering of the states entirely from symmetry arguments. This problem will be addressed in Section 7.4.

is D_{4h} which is a subgroup of O_h . This lowering of the symmetry again results in a splitting of the energy levels, according to

$$T_{2g} \simeq E_g \oplus B_{2g} \quad (7.25)$$

and

$$E_g \simeq A_{1g} \oplus B_{1g} . \quad (7.26)$$

For point groups the command **GTCrystalFieldSplitting** can be used. As shown in Figure 7.3, **GTCrystalFieldSplitting** gives the characters of the irreducible representations of O_h for the classes of D_{4h} as well as the decomposition of these representations into the irreducible representations of D_{4h} . Analogously to **GTCharacterTable** the denotation of the irreducible representation in the output of **GTCrystalFieldSplitting** can be changed by specifying the option **GOIrepNotation**.

Task 25 (Splitting of energy levels in crystal fields). In addition to Example 40, other changes of symmetry will be considered. An axial distortion of a tetrahedron with fixed bond length (tetragonal-tetrahedral distortion) lowers the symmetry to D_{2d} . A distortion of an octahedron along the threefold rotation axis (trigonal distortion) lowers the symmetry to D_{3d} . Use **GTCrystalFieldSplitting** to discuss the splitting of the E_g and T_{2g} levels for the two cases.

7.4

Time-Independent Perturbation Theory

Time-independent perturbation theory	
GTCrystalFieldParameter	Calculates the crystal field parameters for a crystal field expansion
GTCrystalFieldExpansion	Gives the crystal field expansion for a specified symmetry
GTBSTOperator	Calculates matrix elements for the BUCKMASTER–SMITH–THORNLEY operators
GTBSTOperatorElement	Calculates a single matrix element for the BUCKMASTER–SMITH–THORNLEY operators
GTStevensOperator	Calculates matrix elements for the STEVENS operators
GTStevensOperatorElement	Calculates a single matrix element for the STEVENS operators
GTStevensTheta	Gives numerical prefactors for operator equivalents within the crystal field expansion
GTGauntCoefficient	Calculates the integral over three spherical harmonics
GTCFDatabaseInfo	Prints the values of radial integrals saved within a database file
GTCFDatabaseUpdate	Adds new values to a database of radial integrals
GTCFDatabaseRetrieve	Retrieves values from a database of radial integrals

Mathematica

GTAngularMomentumChars, GTCrystalFieldSplitting

First, the point group O_h is installed.

```
In[9]:= Ohgroup = GTInstallGroup[Oh, GOverbose -> False];
characterTableOh =
  GTCharacterTable[Ohgroup, GOIrepNotation -> "Mulliken", GOverbose -> True];
```

	Ee	3 C _{2z}	3 IC _{2x}	6 C _{2x}	6 IC _{4x}	6 IC _{2x}	6 C _{4z}	8 IC _{3x}	8 C _{3y}	IEe
A _{1g}	1	1	1	1	1	1	1	1	1	1
A _{2u}	1	1	-1	-1	1	1	-1	-1	1	-1
A _{1u}	1	1	-1	1	-1	-1	1	-1	1	-1
A _{2g}	1	1	1	-1	-1	-1	-1	1	1	1
E _g	2	2	-2	0	0	0	0	1	-1	-2
E _g	2	2	2	0	0	0	0	-1	-1	2
T _{1g}	3	-1	-1	-1	1	-1	1	0	0	3
T _{2g}	3	-1	-1	1	-1	1	-1	0	0	3
T _{1u}	3	-1	1	-1	-1	1	1	0	0	-3
T _{2u}	3	-1	1	1	1	-1	-1	0	0	-3

$$C_1 = \{Ee\}$$

$$C_2 = \{C_{2z}, C_{2y}, C_{2x}\}$$

$$C_3 = \{IC_{2x}, IC_{2y}, IC_{2z}\}$$

$$C_4 = \{C_{2x}, C_{2y}, C_{2z}, C_{2x}, C_{2y}, C_{2z}\}$$

$$C_5 = \{IC_{4x}, IC_{4x}^3, IC_{4y}, IC_{4y}^3, IC_{4z}, IC_{4z}^3\}$$

$$C_6 = \{IC_{2x}, IC_{2y}, IC_{2z}, IC_{2x}, IC_{2y}, IC_{2z}\}$$

$$C_7 = \{C_{4x}^2, C_{4y}^2, C_{4z}^2, C_{4x}^2, C_{4y}^2, C_{4z}^2\}$$

$$C_8 = \{IC_{3x}, IC_{3y}, IC_{3z}, IC_{3x}^2, IC_{3y}^2, IC_{3z}^2, IC_{3x}, IC_{3y}, IC_{3z}\}$$

$$C_9 = \{C_{3x}, C_{3y}, C_{3z}, C_{3x}^2, C_{3y}^2, C_{3z}^2, C_{3x}, C_{3y}, C_{3z}\}$$

$$C_{10} = \{IEe\}$$

The characters χ^d of the d electrons within the group $O(3)$ are calculated using GTAngularMomentumChars.

```
In[11]:= xdOh = GTAngularMomentumChars[characterTableOh[[1]], 2]
Out[11]:= {5, 1, 1, 1, -1, 1, -1, -1, -1, 5}
```

Since the five dimensional representation D^2 is reducible for O_h symmetry the energy level will split. GTIrep is used to find the irreducible representations.

```
In[12]:= GTIrep[xdOh, characterTableOh];
Eg ⊕ T2g
```

The irreducible representations of O_h are reducible if the group D_{4h} is considered. The decomposition into irreducible representations of D_{4h} is verified by using GTCrystalFieldSplitting.

```
In[13]:= D4hgroup = GTInstallGroup[D4h, GOverbose -> False];
GTCrystalFieldSplitting[Ohgroup, D4hgroup]
```

Repr. in group 1	Ee	C _{2y}	IC _{2x}	C _{2b}	IC _{2a}	IC _{4z}	C _{4x} ¹	IEe	C _{2x}	IC _{2z}	Splitting in group 2
A _{1g}	1	1	1	1	1	1	1	1	1	1	A _{1g}
A _{2u}	1	1	-1	-1	1	1	-1	-1	1	-1	B _{1u}
A _{1u}	1	1	-1	1	-1	-1	1	-1	1	-1	A _{1u}
A _{2g}	1	1	1	-1	-1	-1	-1	1	1	1	B _{1g}
E _g	2	2	-2	0	0	0	0	-2	2	-2	B _{1u} ⊕ A _{1u}
E _g	2	2	2	0	0	0	0	2	2	2	A _{1g} ⊕ B _{1g}
T _{1g}	3	-1	-1	-1	-1	1	1	3	-1	-1	A _{2g} ⊕ E _g
T _{2g}	3	-1	-1	1	1	-1	-1	3	-1	-1	B _{2g} ⊕ E _g
T _{1u}	3	-1	1	-1	1	-1	1	-3	-1	1	A _{2u} ⊕ E _u
T _{2u}	3	-1	1	1	-1	1	-1	-3	-1	1	B _{2u} ⊕ E _u

Figure 7.3 Application of GTAngularMomentumChars, GTIrep, and GTCrystalFieldSplitting to estimate the splitting of d -states in crystal fields.

7.4.1

General Formalism

For a time-independent HAMILTON operator $\hat{H}$ the SCHRÖDINGER equation can be written as,

$$\hat{H}(\mathbf{r})\phi_j^p(\mathbf{r}) = E_0^p \phi_j^p(\mathbf{r}), \quad (7.27)$$

where ϕ_j^p denotes an eigenfunction that transforms as a basis function of the irreducible representation Γ^p of the associated group of the SCHRÖDINGER equation²⁾ $\mathcal{G}$.

By perturbing the HAMILTON operator $\hat{H}$ with an external potential $\hat{V}$, the SCHRÖDINGER equation reads

$$(\hat{H}(\mathbf{r}) + \hat{V}(\mathbf{r}))\psi_l^r(\mathbf{r}) = E^r \psi_l^r(\mathbf{r}). \quad (7.28)$$

In general, the symmetry of the system gets lowered due to the influence of $\hat{V}$. The group of the SCHRÖDINGER equation $\mathcal{G}'$ for equation (7.28) has to be a subgroup of $\mathcal{G}$ ³⁾,

$$\mathcal{G}' \subset \mathcal{G}. \quad (7.29)$$

The functions $\psi_l^r(\mathbf{r})$, $l = 1, \dots, l_r$, are basis functions of an irreducible representation $\Gamma^{r'}$ of $\mathcal{G}'$. As discussed in Section 7.3, it can be expected that the l_p -fold degenerate energy level E_0^p splits into several states with lower degeneracy, depending on the decomposition of Γ^p into irreducible representations $\Gamma^{r'}$ of $\mathcal{G}'$,

$$\Gamma^p \simeq n_1 \Gamma^{1'} \oplus \dots \oplus n_M \Gamma^{M'}. \quad (7.30)$$

Here, M denotes the number of inequivalent irreducible representations of $\mathcal{G}'$. In linear perturbation theory, the level E^r can be approximated by

$$E^r \approx E_0^p + \Delta E^r, \quad (7.31)$$

where ΔE^r can be calculated from the eigenvalues of the matrix $\underline{A}$ with entries,

$$A_{ij}^p = \left(\phi_i^p, \hat{V} \phi_j^p \right). \quad (7.32)$$

$\underline{A}$ has as much distinct eigenvalues as irreducible representations occur on the right-hand side of the decomposition in (7.30).

Since, $\hat{V}(\mathbf{r})$ is a linear operator having the symmetry of a subgroup of $\mathcal{G}$, it can be expressed as a linear combination of irreducible tensor operators $\hat{Q}_k^q$, transforming as one of the N inequivalent irreducible representations Γ^q of $\mathcal{G}$,

$$\hat{V}(\mathbf{r}) = \sum_{q=1}^N \sum_{k=1}^{l_q} Q_k^q(\mathbf{r}). \quad (7.33)$$

2) For brevity $\mathcal{G}$ is used instead of $\mathcal{G}_{\text{SEQ}}$.

3) Also, perturbations are possible that do not break the initial symmetry of a system, i.e., $\mathcal{G}' = \mathcal{G}$. These perturbations will change the values of the energy levels, but do not change their degeneracy.

Combining the equations (7.32) and (7.33), the entries of the matrix $\underline{A}$ can be calculated via

$$A_{ij}^p = \sum_{q=1}^N \sum_{k=1}^{l_q} \left(\phi_i^p, Q_k^q \phi_j^p \right). \quad (7.34)$$

By applying the WIGNER-ECKART Theorem, one finally ends up with

$$A_{ij}^p = \sum_{q=1}^N \sum_{k=1}^{l_q} \sum_{\alpha=1}^{n_p} \left(p \begin{matrix} q & q \\ i & k \end{matrix} \middle| p, \alpha \right)^* \left(p | \hat{Q}^q | p \right)_\alpha. \quad (7.35)$$

In the above equation n_p denotes the number of times the irreducible representation Γ^p occurs within the direct product representation $\Gamma^q \otimes \Gamma^p$. By applying the WIGNER-ECKART Theorem, the matrix element $\left(p | \hat{Q}^q | p \right)_\alpha$ has to be calculated once for every irreducible representation. All other matrix elements can be calculated from the CLEBSCH-GORDAN coefficients, which are in most cases computationally less expensive to obtain.

7.4.2

Crystal Field Expansion

Crystal field theory represents a semiempirical approach to describe localized states in an atomic or crystallographic surrounding based on perturbation theory. In Example 40, the splitting of energy levels due to the influence of a crystal field was discussed qualitatively. For a quantitative approach in the framework of linear perturbation theory, an effective crystal field Hamiltonian can be formulated where the crystal field $V_{\text{cr}}(\mathbf{r})$ is assumed to be small,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) + V_{\text{cr}}(\mathbf{r}) \right] \phi(\mathbf{r}) = E \phi(\mathbf{r}). \quad (7.36)$$

The crystal field itself is given by the electrostatic potential of its neighborhood where $\rho(\mathbf{r}')$ represents the charge density of the surrounding atoms, e is the elementary charge, and ϵ_0 is the vacuum permittivity,

$$V_{\text{cr}}(\mathbf{r}) = -\frac{e}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}'. \quad (7.37)$$

For $r < r'$, the integrand can be expanded in terms of LEGENDRE polynomials P_l ,

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{r' \sqrt{1 - 2 \frac{r}{r'} \cos \beta + \left(\frac{r}{r'} \right)^2}} = \frac{1}{r'} \sum_{l=0}^{\infty} \left(\frac{r}{r'} \right)^l P_l(\cos \beta). \quad (7.38)$$

In the above equation, β is the angle between $\mathbf{r}$ and $\mathbf{r}'$ ($r r' \cos \beta = \mathbf{r} \cdot \mathbf{r}'$). Furthermore, in spherical polar coordinates $\mathbf{r} = (r, \theta, \phi)$ and $\mathbf{r}' = (r', \theta', \phi')$, the addition

theorem for spherical harmonics can be applied,

$$P_l(\cos \beta) = \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_l^m(\theta', \phi')^* Y_l^m(\theta, \phi). \quad (7.39)$$

As a consequence, the electrostatic potential can be written as an expansion in terms of spherical harmonics

$$V_{\text{cr}}(r, \theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l A_l^m r^l Y_l^m(\theta, \phi), \quad (7.40)$$

where A_l^m is called the crystal field parameter,

$$A_l^m = -\frac{1}{2l+1} \frac{e}{\epsilon_0} \int d^3\mathbf{r}' \frac{\rho(\mathbf{r}')}{r'^{l+1}} Y_l^m(\theta', \phi')^*. \quad (7.41)$$

For a central atom surrounded by N ligands the so-called point charge model can be constructed, where the charge distribution is given by

$$\rho(\mathbf{r}') = \sum_{i=1}^N q_i \delta(\mathbf{R}_i - \mathbf{r}'). \quad (7.42)$$

For the point charge model, the crystal field parameters can be evaluated analytically by plugging (7.42) into (7.41), giving

$$A_l^m = -\frac{1}{2l+1} \frac{e}{\epsilon_0} \sum_{i=1}^N q_i \frac{Y_l^m(\Theta_i, \Phi_i)}{R_i^{l+1}}. \quad (7.43)$$

Here, Θ_i , Φ_i , and R_i refer to the vectors $\mathbf{R}_i$ in (7.42), as $\mathbf{R}_i = (R_i, \Theta_i, \Phi_i)$. Since some of the crystal field parameters are zero, the expansion of the crystal field in terms of spherical harmonics can be simplified. The HAMILTON operator is invariant under all transformations of the group of the SCHRÖDINGER equation $\mathcal{G}_{\text{SEQ}}$. Analogously, the same holds for the crystal field. Hence, the crystal field expansion has to be invariant under the application of the character projection operator of the identity representation Γ^1 ,

$$\hat{P}^1 V_{\text{cr}}(r, \theta, \phi) = V_{\text{cr}}(r, \theta, \phi). \quad (7.44)$$

However, for any transformation $\hat{P}(T) \in \mathcal{G}_{\text{SEQ}}$, the spherical harmonics transform as

$$\hat{P}(T) Y_l^m = \sum_{m'=-l}^l D_{m'm}^l(T) Y_l^{m'}, \quad (7.45)$$

where $D_{m'm}^l(T)$ denotes the WIGNER-D function. By calculating the left-hand side of equation (7.44) explicitly, an expansion in terms of transformed parameters $\tilde{A}_l^{m'}$

can be obtained,

$$\begin{aligned}
 P^1 V_{\text{cr}}(r, \theta, \phi) &= \sum_{l=0}^{\infty} \sum_{m'=-l}^l r^l \underbrace{\frac{1}{g} \sum_{m=-l}^l A_l^m \sum_{T \in \mathcal{G}} D_{m'm}^l(T)}_{\tilde{A}_l^{m'}} Y_l^{m'}(\theta, \phi) \\
 &= \sum_{l=0}^{\infty} \sum_{m'=-l}^l r^l \tilde{A}_l^{m'} Y_l^{m'}(\theta, \phi). \quad (7.46)
 \end{aligned}$$

By making use of (7.40) and (7.44) and comparing coefficients it follows that $A_l^m = \tilde{A}_l^m$, which leads to the following system of linear equations

$$A_l^m = \frac{1}{g} \sum_{T \in \mathcal{G}} \sum_{m'=-l}^l D_{mm'}^l(T) A_l^{m'}. \quad (7.47)$$

Since (7.47) is under-determined it is not possible to obtain a solution for every A_l^m . However, it is possible to verify which parameters vanish. Equation (7.47) is used in the command **GTCrystalField**.

Example 41 (Octahedral, tetrahedral, and cubic crystal fields). In Example 40, it was shown that the electronic d -states split into states associated to the irreducible representations T_{2g} and E_g for a crystal field with O_h symmetry. With the help of GTPack the splitting of d -states within an octahedral (O_h), a cubic (O_h), and a tetrahedral (T_d) crystal field can be calculated explicitly, as demonstrated

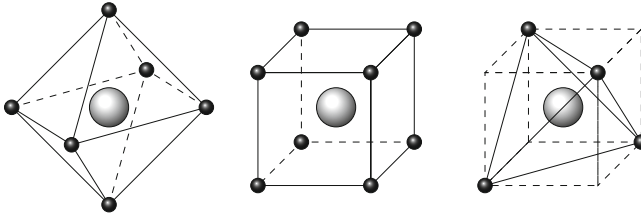


Figure 7.4 Illustration of an octahedral, a cubic, and a tetrahedral crystal field.

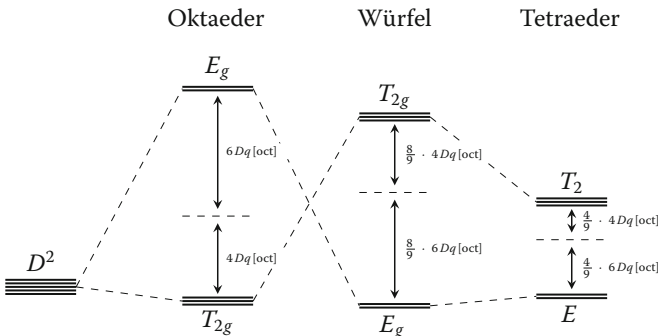


Figure 7.5 Splitting of the electronic d -state in an octahedral, a cubic and a tetrahedral field.

in Figure 7.5 (refer to Figure 7.4 for an illustration of the crystal field). The *Mathematica* example can be found in Figure 7.6. To obtain the crystal field expansion according to (7.40), the command **GTCrystalField** can be used. The crystal field expansion up to $l = 4$ is similar for the point groups O_h and T_d . To calculate ma-

Mathematica

GTCrystalField, GTCrystalFieldParameter, GTGauntCoefficient

To calculate the crystal field Hamiltonian by means of GTCrystalField, the point group (O_h) has to be installed.

```
In[9]:= Ohgroup = GTInstallGroup[Oh, GOverbose -> "False"];
vcr = GTCrystalField[Ohgroup, 4]
```

```
Out[10]:= A[0, 0] Y[0, 0] + r^4 A[4, 4] Y[4, -4] +  $\sqrt{\frac{14}{5}}$  r^4 A[4, 4] Y[4, 0] + r^4 A[4, 4] Y[4, 4]
```

According to linear perturbation theory the matrix $A_{m_1, m_2}^l = (Y_l^{m_1}, V_{cr} Y_l^{m_2})$ needs to be constructed. This can be simplified by using GTGauntCoefficient.

```
In[11]:= Amat = vcr /. Y[l_, m_] ->
Table[(-1)^m1 GTGauntCoefficient[2, -m1, 1, m, 2, m2], {m1, -2, 2}, {m2, -2, 2}];
```

In the following the eigenvalues for an octahedral, a cubic and a tetrahedral crystal field will be calculated. According to the literature the parameters Dq[oct] and e[oct] are introduced.

```
In[12]:= rule = {q x^4 -> 24 π Dq[oct], q -> 2 / 3 π e[oct]};
```

Octahedron

```
In[13]:= Roct = {{R, 0, 0}, {-R, 0, 0}, {0, R, 0}, {0, -R, 0}, {0, 0, R}, {0, 0, -R}} /. R -> 1;
```

```
In[14]:= qoct = Table[q, {i, 1, 6}];
```

```
In[15]:= Expand[Eigenvalues[Amat]] /.
A[l_, m_] -> GTCrystalFieldParameter[l, m, Roct, qoct] /. rule
```

```
Out[15]:= {-4 Dq[oct] + e[oct], -4 Dq[oct] + e[oct],
-4 Dq[oct] + e[oct], 6 Dq[oct] + e[oct], 6 Dq[oct] + e[oct]}
```

Cube

```
In[16]:= Rcube = {{R, R, R}, {-R, R, R}, {-R, -R, R}, {R, -R, R},
{R, R, -R}, {-R, R, -R}, {-R, -R, -R}, {R, -R, -R}} / Sqrt[3] /. R -> 1;
```

```
In[17]:= qcube = Table[q, {i, 1, 8}];
```

```
In[18]:= Expand[Eigenvalues[Amat]] /.
A[l_, m_] -> GTCrystalFieldParameter[l, m, Rcube, qcube] /. rule
```

```
Out[18]:= { $\frac{32 Dq[oct]}{9} + \frac{4 e[oct]}{3}, \frac{32 Dq[oct]}{9} + \frac{4 e[oct]}{3},$ 
 $\frac{32 Dq[oct]}{9} + \frac{4 e[oct]}{3}, -\frac{16 Dq[oct]}{3} + \frac{4 e[oct]}{3}, -\frac{16 Dq[oct]}{3} + \frac{4 e[oct]}{3}$ }
```

Tetrahedron

```
In[19]:= Rtet = {{R, -R, R}, {-R, R, R}, {-R, -R, -R}, {R, R, -R}} / Sqrt[3] /. R -> 1;
```

```
In[20]:= qtet = Table[q, {i, 1, 4}];
```

```
In[21]:= Expand[Eigenvalues[Amat]] /.
A[l_, m_] -> GTCrystalFieldParameter[l, m, Rtet, qtet] /. rule
```

```
Out[21]:= { $\frac{16 Dq[oct]}{9} + \frac{2 e[oct]}{3}, \frac{16 Dq[oct]}{9} + \frac{2 e[oct]}{3},$ 
 $\frac{16 Dq[oct]}{9} + \frac{2 e[oct]}{3}, -\frac{8 Dq[oct]}{3} + \frac{2 e[oct]}{3}, -\frac{8 Dq[oct]}{3} + \frac{2 e[oct]}{3}$ }
```

Figure 7.6 Calculation of the crystal field splitting of the electronic d -state in an octahedral, a cubic, and a tetrahedral field using GTPack (cf. Figure 7.5).

trix elements over the crystal field potential (see (7.34)) the wave functions are assumed to have the form,

$$\phi_l^m = R_l(r)Y_l^m(\theta, \phi). \quad (7.48)$$

Hence, an integral over three spherical harmonics has to be evaluated, which can be done using the command **GTGauntCoefficient**. The splitting ΔE for each state can be found by taking the eigenvalues of the matrix $\underline{\underline{A}}$ of equation (7.34). According to the common notation in the literature, the quantities $Dq[\text{OCT}]$ and $e[\text{OCT}]$ are introduced. The splitting between the T_{2g} and the E_g state is found to be $10Dq[\text{OCT}]$ for an octahedral field and $8/9 \cdot 10Dq[\text{OCT}]$ for a cubic crystal field. Furthermore, the ordering of the levels change. Whereas E_g is higher than T_{2g} for a positively charged octahedral crystal field, E_g is lower in energy for a positively charged cubic crystal field. This ordering remains for tetrahedral fields, where the level E is lower in energy than the level T_2 (for T_d there is no inversion symmetry and hence no distinction between even (g) and odd (u) irreducible representations). The total splitting of $4/9 \cdot 10Dq[\text{OCT}]$ is less in comparison to the octahedral and the cubic field.

Task 26 (Trigonal crystal fields). Trigonal crystal fields having C_{3v} symmetry can occur on the surfaces of fcc crystals. How do p -states split? Verify the crystal field expansion for this symmetry.

7.4.3

Crystal Field Operators

The goal of crystal field theory is to determine the interaction of localized and unpaired electrons within a nonspherical crystal environment. The separation of atomic wave functions into a spherical and a radial part motivates the idea of expanding the crystal field in terms of spherical harmonics, as presented in the previous section. This concept can be generalized by expanding the crystal field in terms of crystal field operators. In general, such crystal field operators are spherical tensor operators $\hat{T}_l^m$ ($-l \leq m \leq l$), which are supposed to transform in the same way as the spherical harmonics,

$$\hat{P}(T)\hat{T}_l^m\hat{P}^{-1}(T) = \sum_{m'=-l}^l D_{m'm}^l(T)\hat{T}_l^{m'}. \quad (7.49)$$

Furthermore, they have to fulfill the following commutation relations with the total angular momentum operators,

$$[\hat{J}_\pm, \hat{T}_l^m] = \hbar \sqrt{(l \mp m)(l \pm m + 1)} \hat{T}_l^{m \pm 1}, \quad (7.50)$$

and

$$[\hat{J}_z, \hat{T}_l^m] = \hbar m \hat{T}_l^m. \quad (7.51)$$

Here $\hat{J}_+ = \hat{J}_x + i\hat{J}_y$ and $\hat{J}_- = \hat{J}_x - i\hat{J}_y$ are the so-called ladder operators. A large amount of definitions for crystal field operators are present within the literature. In summary, these definitions can be distinguished by two basic properties. First, it is possible to define operators in analogy to an expansion of the crystal field in terms of complex spherical harmonics or in terms of real-valued tesseral harmonics. Second, one distinguishes between operators that depend on the polar angles θ and ϕ (which are mainly spherical harmonics with prefactors), and so-called operator equivalents that are linear combinations of angular momentum operators acting on many-particle states. In the following, a brief review of the most important operators is given⁴⁾.

A definition of crystal field operators based on normalized spherical harmonics was suggested by WYBOURNE [111], who introduced the operators⁵⁾

$$\hat{C}_m^{(l)}(\theta, \phi) = \sqrt{\frac{4\pi}{2l+1}} Y_l^m(\theta, \phi). \quad (7.52)$$

The resulting crystal field expansion is expressed via

$$V_{\text{cr}}(r, \theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l B_{lm} \hat{C}_m^{(l)}(\theta, \phi). \quad (7.53)$$

The crystal field parameters B_{lm} are related to the parameters A_l^m of equation (7.40) by

$$B_{lm} = \sqrt{\frac{2l+1}{4\pi}} A_l^m \langle r^l \rangle, \quad (7.54)$$

where $\langle r^l \rangle$ denotes the expectation value of r^l , which can be calculated by integration of the radial part of the unperturbed wave function multiplied by r^l .

A form of crystal field parameters related to spherical harmonics, but based on angular momentum operators are given by the BUCKMASTER-SMITH-THORNLEY operator equivalents $\hat{O}_m^{(l)}$ (BST operators) [112],

$$V_{\text{cr}}(r, \theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \tilde{B}_m^l \hat{O}_m^{(l)}. \quad (7.55)$$

The operators are chosen such that the transformation matrix $\underline{D}$ on the right-hand side of equation (7.49) is similar to the one for the complex spherical harmonics, which is the WIGNER-D matrix. They can be obtained intuitively by calculating the WYBOURNE operators in Cartesian form and by replacing x/r , y/r , and z/r by the angular momentum operators J_x , J_y , and J_z properly taking into account the

4) More detailed information can be found e.g., in the book by MULAK and GAJEK [109] or the report by DANIELSEN and LINDGÅRD [110].

5) The reader has to be careful about the notation. Different operators within the literature are often denoted with the same character. Sometimes, they can be distinguished from the order of l and m in sub- and superscripts.

Table 7.1 List of BST operator equivalents for a cubic crystal field according to Ref. [112]. The abbreviation $X = J(J + 1)$ is used.

l	m	BST operator equivalents
0	0	1
4	0	$\frac{1}{8} \left[35\hat{J}_z^4 - (30X - 25)\hat{J}_z^2 + 3X^2 - 6X \right]$
4	± 4	$\sqrt{\frac{35}{128}} \hat{J}_z^{\pm 4}$
6	0	$\frac{1}{16} \left[231\hat{J}_z^6 - (315X - 735)\hat{J}_z^4 + (105X^2 - 525X + 294)\hat{J}_z^2 - 5X^3 + 40X^2 - 60X \right]$
6	± 4	$\sqrt{\frac{63}{512}} \frac{1}{2} \left[\left(11\hat{J}_z^2 - X - 38 \right) \hat{J}_z^{\pm 4} + \hat{J}_z^{\pm 4} \left(11\hat{J}_z^2 - X - 38 \right) \right]$

commutation relations⁶⁾. A list of some operators $\hat{O}_m^{(l)}$ can be found in Table 7.1. Furthermore, SMITH and THORNLEY [112] gave an expression for the calculation of matrix elements of BST operators that is implemented within the GTPack commands **GTBSTOperator** and **GTBSTOperatorElement**,

$$\langle jm' | \hat{O}_m^{(l)} | jm'' \rangle = (-1)^{j-m'} \begin{pmatrix} j & l & j \\ m' & m & m'' \end{pmatrix} \langle jm' | \hat{O}^{(l)} | jm'' \rangle \quad (7.56)$$

with the reduced matrix element

$$\langle jm' | \hat{O}^{(l)} | jm'' \rangle = \frac{1}{2^l} \sqrt{\frac{(2j+l+1)!}{(2j-l)!}}. \quad (7.57)$$

The symbol $\begin{pmatrix} j & l & j \\ m' & m & m'' \end{pmatrix}$ denotes the WIGNER $3J$ -symbol, which can be evaluated in *Mathematica* by using the command **ThreeJSymbol**.

A similar kind of crystal field parameters as the BST operators, but related to tesseral harmonics, is given by the STEVENS operator equivalents $\hat{O}_m^l$ [113],

$$V_{\text{cr}}(r, \theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l B_m^l \hat{O}_m^l. \quad (7.58)$$

Matrix elements for the STEVENS operator equivalents can be calculated using the commands **GTStevensOperator** and **GTStevensOperatorElement**. For both the STEVENS as well as the BST operators, the angular momentum operators act on many-particle states. Therefore, the crystal field expansion has to take into account the multiplet contribution according to the electronic configuration of the central atom. Such prefactors θ_l were introduced by STEVENS [113]. A list of factors θ_l for rare-earth atoms can be found in Table 7.2. These prefactors can be obtained within GTPack by using the command **GTStevensTheta**. The crystal field parameters B_m^l are given by

$$B_m^l = \theta_l C_l^m A_l^m \langle r^l \rangle, \quad (7.59)$$

6) This scheme goes back to STEVENS [113].

Table 7.2 List of the prefactors θ_l for rare-earth elements (cf. Ref. [113]).

Ion	Configuration		θ_2	θ_4	θ_6
Ce ³⁺	4 <i>f</i> ¹	² F _{5/2}	-2/35	2/7×45	0
Pr ³⁺	4 <i>f</i> ²	³ H ₄	-52/11×15 ²	-4/55×33×3	-17×16/7×11 ² ×13×5×3 ⁴
Nd ³⁺	4 <i>f</i> ³	⁴ I _{9/2}	-7/33×33	-8×17/11×11×13×297	-17×19×5/13 ² ×11 ³ ×3 ³ ×7
Pm ³⁺	4 <i>f</i> ⁴	⁵ F ₄	14/11×11×15	952/13×3 ³ ×11 ³ ×5	2584/11 ² ×13 ² ×3×63
Sm ³⁺	4 <i>f</i> ⁵	⁶ H _{5/2}	13/7×45	26/33×7×45	0
Eu ³⁺	4 <i>f</i> ⁶	⁷ F ₀	0	0	0
Gd ³⁺	4 <i>f</i> ⁷	⁸ S	0	0	0
Tb ³⁺	4 <i>f</i> ⁸	⁷ F ₆	-1/99	2/11×1485	-1/13×33×2079
Dy ³⁺	4 <i>f</i> ⁹	⁶ H _{15/2}	-2/9×35	-8/11×45×273	4/11 ² ×13 ² ×3 ³ ×7
Ho ³⁺	4 <i>f</i> ¹⁰	⁵ I ₈	-1/30×15	-1/11×2730	-5/13×33×9009
Er ³⁺	4 <i>f</i> ¹¹	⁴ I _{15/2}	4/45×35	2/11×15×273	8/13 ² ×11 ² ×3 ³ ×7
Tu ³⁺	4 <i>f</i> ¹²	³ H ₆	1/99	8/3×11×1485	-5/13×33×2079
Yb ³⁺	4 <i>f</i> ¹³	² F _{7/2}	2/63	-2/77×15	4/13×33×63

where C_l^m are the normalization coefficients of the tesseral harmonics and A_l^m are the crystal field parameters of equation (7.41).

Example 42 (Radial integrals). Separating the wave functions into an angular and a radial part (like in equation (7.48)) allows for the introduction of spherical tensor operators as discussed within this section. After having discussed the angular part so far, it remains to deal with the radial part. The crystal field expansion (7.40) contains terms r^l . By calculating matrix elements according to (7.32), expectation values like

$$\langle r^l \rangle = \int_0^\infty dr r^{l+2} |R_l(r)|^2 \quad (7.60)$$

occur. Such expectation values are material specific. The radial wave function can be obtained from *ab initio* methods, e.g., based on density functional theory. Results of such calculations can be found within the literature, e.g., FORSTREUTER *et al.* [114]. Within GTPack it is possible to store specific values to a database and to load them if necessary. To build up or to update a database, the command **GTCFDatabaseUpdate** can be used, which provides an interactive interface. Vice versa, parameters can be retrieved by **GTCFDatabaseRetrieve**. The content of a specified database can be illustrated using **GTCFDatabaseInfo**. An example for retrieving parameters from a database is shown in Figure 7.7.

Example 43 (Stevens operators). The goal of the example is to illustrate the calculation of matrix elements of STEVENS operator equivalents,

$$\langle Jm_1 | \hat{\mathcal{O}}_m^l | Jm_2 \rangle. \quad (7.61)$$

Mathematica

GTCFDatabaseInfo, GTCFDatabaseRetrieve

```
In[9]:= SetDirectory[NotebookDirectory[]];
```

Print the content of a file "radial_integrals.parm" containing radial integrals.

```
In[10]:= GTCFDatabaseInfo["radial_integrals"]
```

	Reference	$\langle r^2 \rangle$	$\langle r^4 \rangle$	$\langle r^6 \rangle$	$\langle r^{-3} \rangle$
Ce_SIC	J. Forstreuter, et al., Phys. Rev. B, 55, 15, 1997	1.34	4.22	25.4	4.55
Dy_SIC	J. Forstreuter, et al., Phys. Rev. B, 55, 15, 1997	0.79	1.55	6.21	9.9
Er_SIC	J. Forstreuter, et al., Phys. Rev. B, 55, 15, 1997	0.724	1.33	5.15	11.5
Eu_SIC	J. Forstreuter, et al., Phys. Rev. B, 55, 15, 1997	0.925	2.06	9.11	7.69
Gd_SIC	J. Forstreuter, et al., Phys. Rev. B, 55, 15, 1997	0.872	1.84	7.79	8.4
Ho_SIC	J. Forstreuter, et al., Phys. Rev. B, 55, 15, 1997	0.756	1.43	5.3	10.7
Lu_SIC	J. Forstreuter, et al., Phys. Rev. B, 55, 15, 1997	0.65	1.11	4.2	14.1
Nd_SIC	J. Forstreuter, et al., Phys. Rev. B, 55, 15, 1997	1.14	3.04	15.8	5.73
Pm_SIC	J. Forstreuter, et al., Phys. Rev. B, 55, 15, 1997	1.06	2.64	13.	6.35
Pr_SIC	J. Forstreuter, et al., Phys. Rev. B, 55, 15, 1997	1.23	3.55	19.8	5.13
Sm_SIC	J. Forstreuter, et al., Phys. Rev. B, 55, 15, 1997	0.986	2.32	10.8	7.01
Tb_SIC	J. Forstreuter, et al., Phys. Rev. B, 55, 15, 1997	0.829	1.68	6.91	9.14
Tm_SIC	J. Forstreuter, et al., Phys. Rev. B, 55, 15, 1997	0.695	1.24	4.72	12.4
Yb_SIC	J. Forstreuter, et al., Phys. Rev. B, 55, 15, 1997	0.669	1.16	4.39	13.3

Retrieve the radial integrals e.g. for Ho.

```
In[11]:= GTCFDatabaseRetrieve["radial_integrals", "Ho_SIC"]
```

```
Out[11]:= {r^2 -> 0.756, r^4 -> 1.43, r^6 -> 5.3, 1/r^3 -> 10.7}
```

Figure 7.7 Example of illustrating and retrieving radial expectation values $\langle r^l \rangle$ from a database in GTPack.

For the example, let's focus on the operator

$$\hat{\mathcal{O}}_3^3 = \frac{1}{4} \left[\hat{J}_z \left(\hat{J}_+^3 + \hat{J}_-^3 \right) + \left(\hat{J}_+^3 + \hat{J}_-^3 \right) \hat{J}_z \right]. \quad (7.62)$$

As can be seen, it is a term based on the ladder operators $\hat{J}_\pm$ and $\hat{J}_z$. The actions of these operators on eigenfunctions of $\hat{J}_z$ and $\hat{J}^2$ are given by

$$\hat{J}_z |Jm\rangle = m |Jm\rangle, \quad (7.63)$$

$$\hat{J}_\pm |Jm\rangle = \sqrt{(J \mp m)(J \pm m + 1)} |Jm \pm 1\rangle. \quad (7.64)$$

For example, taking the vectors $|33\rangle$ and $|30\rangle$ one obtains,

$$\hat{\mathcal{O}}_3^4 |33\rangle = 9\sqrt{5} |30\rangle \quad (7.65)$$

and

$$\hat{\mathcal{O}}_3^4 |30\rangle = 9\sqrt{5} (|33\rangle - |3-3\rangle). \quad (7.66)$$

Hence, it follows

$$\langle 33 | \hat{\mathcal{O}}_3^4 | 33 \rangle = 0, \quad (7.67)$$

Mathematica**GTStevensOperator, GTStevensOperatorElement**

At first, single matrix elements are calculated:

```
In[9]:= GTStevensOperatorElement[4, 3, 3, 3, 3]
```

```
Out[9]= 0
```

```
In[10]:= GTStevensOperatorElement[4, 3, 3, 0, 3]
```

```
Out[10]= 9  $\sqrt{5}$ 
```

```
In[11]:= GTStevensOperatorElement[4, 3, 3, 0, 0]
```

```
Out[11]= 0
```

```
In[12]:= GTStevensOperatorElement[4, 3, 3, 3, 0]
```

```
Out[12]= 9  $\sqrt{5}$ 
```

The full matrix is calculated using GTStevensOperator.

```
In[13]:= GTStevensOperator[4, 3, 3] // MatrixForm
```

```
Out[13]/MatrixForm=
```

$$\begin{pmatrix} 0 & 0 & 0 & -9\sqrt{5} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -3\sqrt{10} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 3\sqrt{10} & 0 \\ -9\sqrt{5} & 0 & 0 & 0 & 0 & 0 & 9\sqrt{5} \\ 0 & -3\sqrt{10} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 3\sqrt{10} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 9\sqrt{5} & 0 & 0 & 0 \end{pmatrix}$$

Figure 7.8 Calculation of matrix elements of STEVENS operator equivalents.

$$\langle 30 | \hat{\mathcal{O}}_3^4 | 33 \rangle = 9\sqrt{5}, \quad (7.68)$$

$$\langle 30 | \hat{\mathcal{O}}_3^4 | 30 \rangle = 0, \quad (7.69)$$

and

$$\langle 3 \pm 3 | \hat{\mathcal{O}}_3^4 | 30 \rangle = \pm 9\sqrt{5}. \quad (7.70)$$

Such matrix elements can be evaluated automatically using the command **GTStevensOperatorElement**. To obtain the full matrix, the command **GTStevensOperator** can be used. A GTPack example is shown in Figure 7.8.

7.5

Transition Probabilities and Selection Rules

At zero temperature, a quantum mechanical system remains in the ground state. The system can be transferred into an excited state by introducing a time-

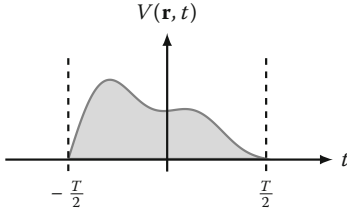


Figure 7.9 A time-dependent perturbation with duration T , starting at $t_0 = -T/2$.

dependent perturbation. Subsequently, the connection between the transition probability and the symmetry of the perturbation is discussed.

The starting point is the time-dependent SCHRÖDINGER equation,

$$i\hbar \frac{\partial}{\partial t} \Phi(\mathbf{r}, t) = [\hat{H}_0(\mathbf{r}) + \hat{V}(\mathbf{r}, t)]\Phi(\mathbf{r}, t), \quad (7.71)$$

where $\hat{H}_0(\mathbf{r})$ represents a stationary Hamiltonian having the symmetry group $\mathcal{G}$ and $\hat{V}(\mathbf{r}, t)$ denotes a weak time-dependent perturbation. As shown in Figure 7.9, it is assumed that the perturbation is switched on at time $t_0 = -T/2$ and lasts for a duration T . Hence, for times $t < -T/2$, the solution of (7.71) is given by the solution of the stationary SCHRÖDINGER equation,

$$\hat{H}_0(\mathbf{r})\phi_n^{p,\alpha}(\mathbf{r}) = E^{p,\alpha}\phi_n^{p,\alpha}(\mathbf{r}). \quad (7.72)$$

According to the matrix element theorem (Theorem 35), the eigenfunctions $\phi_n^{p,\alpha}$, $n = 1, \dots, d_p$ are basis functions belonging to a d_p -dimensional irreducible representation Γ^p of the group of the SCHRÖDINGER equation $\mathcal{G}$. The index α accounts for multiple linearly independent sets of such basis functions. The solution of the perturbed system (7.71) is obtained by expanding Φ in terms of $\phi_n^{p,\alpha}$, including time-dependent coefficients $c_n^{p,\alpha}(t)$ as

$$\Phi(\mathbf{r}, t) = \sum_p \sum_{\alpha} \sum_{n=1}^{d_p} c_n^{p,\alpha}(t) \phi_n^{p,\alpha}(\mathbf{r}) e^{-i \frac{E^{p,\alpha}}{\hbar} t}. \quad (7.73)$$

Plugging (7.73) into (7.71) and using the orthogonality of the functions $\phi_n^{p,\alpha}(\mathbf{r})$, a system of linear differential equations can be obtained, given by

$$i\hbar \frac{\partial}{\partial t} c_m^{q,\beta}(t) = \sum_p \sum_{\alpha} \sum_{n=1}^{d_p} c_n^{p,\alpha}(t) V_{mn}^{q,\beta;p,\alpha}(t) e^{i\omega_{q,\beta;p,\alpha} t}. \quad (7.74)$$

Here, $V_{mn}^{q,\beta;p,\alpha}$ denotes the matrix element

$$V_{mn}^{q,\beta;p,\alpha} = \left(\phi_m^{q,\beta}, \hat{V} \phi_n^{p,\alpha} \right) \quad (7.75)$$

and

$$\omega_{q,\beta;p,\alpha} = \frac{E_{q,\beta} - E_{p,\alpha}}{\hbar}. \quad (7.76)$$

Initially, i.e., before the perturbation starts to interact with the system, the system is in a pure state described by the triple (s, l, γ) . Therefore, the $c_n^{p,\alpha}$ are given by

$$c_n^{p,\alpha}(t) = \delta_{p,s} \delta_{n,l} \delta_{\alpha,\gamma} \quad \text{for } t < -\frac{T}{2}. \quad (7.77)$$

For times $t > T/2$, equation (7.74) can be solved self-consistently by rewriting it in terms of an integral equation. Such an integral equation is obtained by integrating over time on both sides of (7.74) and using the initial condition (7.77),

$$c_m^{q,\beta}(T/2) = \delta_{\alpha,\gamma} \delta_{n,l} \delta_{p,s} - \frac{i}{\hbar} \sum_{n=1}^{d_q} \int_{-T/2}^{T/2} dt c_n^{p,\alpha}(t) V_{mn}^{q,\beta;p,\alpha}(t) e^{i\omega_{q,\beta;p,\alpha} t}. \quad (7.78)$$

The quantity $|c_m^{q,\beta}|^2$ describes the probability of finding the system within the state (q, β, m) with energy $E^{q,\beta}$. In other words, starting within the initial state (s, l, γ) , the probability for the transition $(s, l, \gamma) \rightarrow (q, \beta, m)$ is given by

$$W_{q,\beta;m}^{s,\gamma;l} = |c_m^{q,\beta}(t)|^2, \quad t \geq \frac{T}{2}. \quad (7.79)$$

In first order, the evaluation of (7.78) gives

$$c_m^{q,\beta(1)}(T/2) = \delta_{q,s} \delta_{\beta,\gamma} \delta_{m,l} - \frac{i}{\hbar} \int_{-T/2}^{T/2} dt V_{ml}^{q,\beta;s,\gamma}(t) e^{i\omega_{q,\beta;s,\gamma} t}. \quad (7.80)$$

In the following, the special case of a periodic perturbation is discussed. To do so, $\hat{V}(\mathbf{r}, t)$ is assumed to have the form

$$\hat{V}(\mathbf{r}, t) = \mathbf{A}(\mathbf{r}) e^{-i\omega t} + \mathbf{A}^\dagger(\mathbf{r}) e^{i\omega t}. \quad (7.81)$$

Using (7.81), the probability for a transition $(s, l, \gamma) \rightarrow (q, \beta, m)$ can be evaluated in first order. Separately, for the two terms in (7.81), the transition probabilities are given by

$$\text{Absorption: } W_{q,\beta;m}^{s,\gamma;l}(\omega) = \frac{2\pi}{\hbar} \left| (\phi_m^{q,\beta}, \mathbf{A} \phi_l^{s,\gamma}) \right|^2 \delta(E^{q,\beta} - E^{s,\gamma} - \hbar\omega). \quad (7.82)$$

and

$$\text{Emission: } W_{q,\beta;m}^{s,\gamma;l}(\omega) = \frac{2\pi}{\hbar} \left| (\phi_m^{q,\beta}, \mathbf{A}^\dagger \phi_l^{s,\gamma}) \right|^2 \delta(E^{q,\beta} - E^{s,\gamma} + \hbar\omega). \quad (7.83)$$

The two quantities refer to transitions incorporating the absorption and emission of an energy $\hbar\omega$. To evaluate (7.82) and (7.83), the main quantities to calculate are the matrix elements $|(\phi_m^{q,\beta}, \mathbf{A} \phi_l^{s,\gamma})|^2$ and $|(\phi_m^{q,\beta}, \mathbf{A}^\dagger \phi_l^{s,\gamma})|^2$. As in the case of

time-independent perturbation theory, $\mathbf{A}$ and $\mathbf{A}^\dagger$ can be written in terms of irreducible tensor operators. The following discussion is concentrated on $\mathbf{A}$ and it is assumed that it transforms as the n^{th} row of the irreducible representation Γ^p of $\mathcal{G}$. According to the WIGNER–ECKART Theorem (Theorem 27), $|\langle \phi_m^{q,\beta}, \mathbf{A} \phi_l^{s,\gamma} \rangle|^2$ can be written as

$$\left| \langle \phi_m^{q,\beta}, \hat{\mathbf{A}} \phi_l^{s,\gamma} \rangle \right|^2 = \sum_{\alpha=1}^{n_r} \left(\begin{matrix} s & p \\ l & n \end{matrix} \middle| \begin{matrix} q, \alpha \\ m \end{matrix} \right)^* (q|p|s)_\alpha^{\beta,\gamma}, \quad (7.84)$$

where $(q|p|s)$ denotes the so-called reduced matrix element and $\left(\begin{matrix} s & p \\ l & n \end{matrix} \middle| \begin{matrix} q, \alpha \\ m \end{matrix} \right)$ the CLEBSCH–GORDAN coefficients. The index $\alpha = 1, \dots, n_q$ accounts for the number of times the irreducible representation Γ^q occurs within the decomposition of the direct product representation $\Gamma^p \otimes \Gamma^s$,

$$\Gamma^p \otimes \Gamma^s \simeq n_1 \Gamma^1 \oplus \dots \oplus n_q \Gamma^q \oplus \dots \quad (7.85)$$

In the case where Γ^q does not occur within the decomposition (7.85), i.e., $n_q = 0$, the transition between states transforming as the irreducible representation Γ^s to states transforming as Γ^q are forbidden for any perturbations transforming as the irreducible representation Γ^p . That means, the discussion of decompositions like (7.85) and the calculation of CLEBSCH–GORDAN coefficients suffices for the formulation of selection rules describing all allowed and forbidden transitions between electronic states.

Example 44 (Optical selection rules for linearly polarized light for the crystallographic point group D_4). As an example, the coupling of an electronic system to a weak electromagnetic field is considered. The Hamiltonian of the system can be written by incorporating the vector potential $\mathbf{A}$ into the canonical momentum as

$$\hat{H} = \frac{1}{2m} (\hat{\mathbf{p}} - e\mathbf{A})^2 + U(\mathbf{r}) \approx \underbrace{\frac{\hat{\mathbf{p}}^2}{2m}}_{\hat{H}_0} + \underbrace{V(\mathbf{r}) - \frac{e}{m} \mathbf{A} \cdot \hat{\mathbf{p}}}_{\hat{V}(\mathbf{r},t)}. \quad (7.86)$$

Because of the weak field, the approximation $\mathbf{A}^2 \approx 0$ is applied. The time-dependent perturbation $\hat{V}(\mathbf{r}, t)$ is given by

$$\hat{V}(\mathbf{r}, t) = -\frac{e}{m} \mathbf{A}(\mathbf{r}, t) \cdot \hat{\mathbf{p}}. \quad (7.87)$$

The vector potential describes a linearly polarized plane wave. The so called dipole approximation is applied. Thus the vector potential is approximated by,

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{A}_0 e^{-i(\mathbf{k} \cdot \mathbf{r} + \omega t)} = \mathbf{A}_0 \left(1 - i\mathbf{k} \cdot \mathbf{r} + \frac{1}{2} (i\mathbf{k} \cdot \mathbf{r})^2 + \dots \right) e^{-i\omega t} \approx \mathbf{A}_0 e^{-i\omega t}. \quad (7.88)$$

In order to calculate matrix elements $\langle \phi_m^{q,\beta}, \mathbf{A}_0 \cdot \hat{\mathbf{p}} \phi_l^{s,\gamma} \rangle$ according to equation (7.82), the momentum operator is expressed in terms of the position operator $\mathbf{r}$.

To do so, the EHRENFEST theorem is applied, thus

$$\hat{\mathbf{p}} = m \frac{d}{dt} \hat{\mathbf{r}} = \frac{im}{\hbar} [\hat{H}_0, \mathbf{r}] . \quad (7.89)$$

Hence, it follows for the matrix elements

$$(\phi_m^{q,\beta}, \mathbf{A}_0 \cdot \hat{\mathbf{p}} \phi_l^{s,\gamma}) = \frac{im}{\hbar} (E^{q,\beta} - E^{s,\gamma}) (\phi_m^{q,\beta}, \mathbf{A}_0 \cdot \mathbf{r} \phi_l^{s,\gamma}) . \quad (7.90)$$

In the following, the evaluation of $(\phi_m^{q,\beta}, \mathbf{A}_0 \cdot \mathbf{r} \phi_l^{s,\gamma})$ is discussed for the point group D_4 having the y -axis as the principle axis. By applying the character projection operator of each irreducible representation of D_4 to the functions $A_{0,x}x$, $A_{0,y}y$ and $A_{0,z}z$ it can be verified that $A_{0,x}x$ and $A_{0,z}z$ belong to the irreducible representation E and $A_{0,y}y$ belongs to the irreducible representation A_2 . Furthermore, with the help of the projection operator of the irreducible representation E it can be seen that $A_{0,x}x$ transforms as the second row and $A_{0,z}z$ as the first row of E . A *Mathematica* example using GTPack is shown in Figure 7.10.

It is assumed that the initial state transforms as the first row of the 2-dimensional representation E . Sticking to a perturbation $A_{0,x}x$ also transforming like the first row of the 2-dimensional irreducible representation E , the associated matrix element can be expressed as

$$(\phi_l^r(\mathbf{r}), A_{0,x}x \phi_1^E(\mathbf{r})) = \left(\begin{matrix} E & E \\ 1 & 1 \end{matrix} \middle| \begin{matrix} r, 1 \\ 1 & 1 \end{matrix} \right)^* (r|E|E) . \quad (7.91)$$

The transition probability can only be nonzero, if the irreducible representation belonging to the final state occurs within the decomposition of the direct product representation $\Gamma^E \otimes \Gamma^E$,

$$\Gamma^E \otimes \Gamma^E \simeq A_1 \oplus A_2 \oplus B_1 \oplus B_2 . \quad (7.92)$$

Therefore, the index r in equation (7.91) denotes one of the one-dimensional representations A_1 , A_2 , B_1 , or B_2 . The decomposition of $\Gamma^E \otimes \Gamma^E$ is calculated by using the command **GTIrep** as shown in Figure 7.12. The CLEBSCH–GORDAN coefficients are calculated by applying the command **GTclebschGordanCoefficients**. Furthermore, they restrict the argument and show that the final state Φ_l^r can only transform as A_1 or B_1 . Similarly, a perturbation of the form $A_{0,z}z$ only allows for transitions of an initial state transforming like the first row of the irreducible representation E into final states transforming like the irreducible representations A_2 or B_2 . A perturbation $A_{0,y}y$ transforming like A_2 leads to a decomposition

$$\Gamma^E \otimes \Gamma^{A_2} \simeq E , \quad (7.93)$$

i.e., an initial state transforming like the irreducible representation E can only be excited into another state transforming like the irreducible representation E . From the CLEBSCH–GORDAN coefficients, it can be seen that an initial state transforming like the first row of the irreducible representation E can only be excited into a final state transforming like the second row of the irreducible representation E . A summary of the allowed transitions is shown in Figure 7.11.

Mathematica

First, the point group and the character table are computed.

```
In[9]:= grp = GTInstallGroup[D4, GVerbose -> False];
ct = {classes, chars, names} = GTCharacterTable[grp, GOIrepNotation -> "Mulliken"];
```

	Ee	2 C _{2z}	2 C _{2d}	2 C _{4y}	C _{2y}
A ₁	1	1	1	1	1
A ₂	1	-1	-1	1	1
B ₂	1	-1	1	-1	1
B ₁	1	1	-1	-1	1
E	2	0	0	0	-2

$C_1 = \{Ee\}$

$C_2 = \{C_{2z}, C_{2x}\}$

$C_3 = \{C_{2d}, C_{2c}\}$

$C_4 = \{C_{4y}, C_{4y}^{-1}\}$

$C_5 = \{C_{2y}\}$

The representation matrices of the irreducible representations are calculated using GTGetIrep.

```
In[11]:= IrA1 = GTGetIrep[grp, 1, ct, GOMethod -> "Cornwell"];
IrA2 = GTGetIrep[grp, 2, ct, GOMethod -> "Cornwell"];
IrB2 = GTGetIrep[grp, 3, ct, GOMethod -> "Cornwell"];
IrB1 = GTGetIrep[grp, 4, ct, GOMethod -> "Cornwell"];
IrE = GTGetIrep[grp, 5, ct, GOMethod -> "Cornwell"];
```

The transformation behavior of possible perturbations is analyzed by applying projection operators.

x

```
In[16]:= Efx[x_, y_, z_] = x;
Simplify[GTCharProjectionOperator[classes, chars, Efx, {x, y, z}]]
```

```
Out[17]= {0, 0, 0, 0, x}
```

x transforms as the second row of the irreducible representation E.

```
In[18]:= Simplify[GTPProjectionOperator[grp, IrE, 2, 2, Efx, {x, y, z}]]
```

```
Out[18]= x
```

y

```
In[19]:= Efy[x_, y_, z_] = y;
Simplify[GTCharProjectionOperator[classes, chars, Efy, {x, y, z}]] // FullSimplify
```

```
Out[20]= {0, y, 0, 0, 0}
```

y transforms as the irreducible representation A₂.

z

```
In[21]:= Efz[x_, y_, z_] = z;
Simplify[GTCharProjectionOperator[classes, chars, Efz, {x, y, z}]]
```

```
Out[22]= {0, 0, 0, 0, z}
```

z transforms as the first row of the irreducible representation E.

```
In[23]:= Simplify[GTPProjectionOperator[grp, IrE, 1, 1, Efz, {x, y, z}]]
```

```
Out[23]= z
```

Figure 7.10 Verify the transformation behavior of the perturbations $A_{0,x}x$, $A_{0,y}y$, and $A_{0,z}z$.

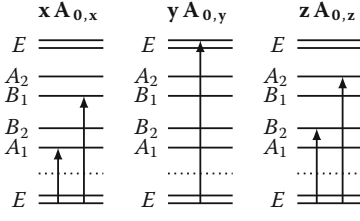


Figure 7.11 Possible transitions of an initial state transforming like the first row of the irreducible representation E of D_4 into a final state transforming like another irreducible representation of D_4 for the perturbations $A_{0,x}x$, $A_{0,y}y$, and $A_{0,z}z$.

Mathematica

Calculate the decomposition of the direct product representations $E \otimes E$ and $E \otimes A_2$.

```
In[24]:= χExE = GTDirectProductChars[chars[[5]], chars[[5]]];
GTIrep[χExE, ct]
```

$A_1 \oplus A_2 \oplus B_2 \oplus B_1$

```
Out[25]:= {1, 1, 1, 1, 0}
```

```
In[26]:= χExA2 = GTDirectProductChars[chars[[5]], chars[[2]]];
GTIrep[χExA2, ct]
```

E

```
Out[27]:= {0, 0, 0, 0, 1}
```

The Clebsch–Gordan coefficients are calculated using `GTCLCLebschGordanCoefficients` and illustrated using `GTCLCLebschGordanTable`.

$E \otimes E$

```
In[28]:= cgk1 = GTCLCLebschGordanCoefficients[IrE, IrE, IrA1];
cgk2 = GTCLCLebschGordanCoefficients[IrE, IrE, IrA2];
cgk3 = GTCLCLebschGordanCoefficients[IrE, IrE, IrB2];
cgk4 = GTCLCLebschGordanCoefficients[IrE, IrE, IrB1];
```

```
In[32]:= GTCLCLebschGordanTable[IrE, IrE, {cgk1, cgk2, cgk3, cgk4}, {"A1", "A2", "B2", "B1"}]
```

		A1	A2	B2	B1
j	k	1	1	1	1
1	1	$\frac{1}{\sqrt{2}}$	0	0	$-\frac{1}{\sqrt{2}}$
1	2	0	$-\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0
2	1	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0
2	2	$\frac{1}{\sqrt{2}}$	0	0	$\frac{1}{\sqrt{2}}$

$E \otimes A_2$

```
In[33]:= cgk5 = GTCLCLebschGordanCoefficients[IrE, IrA2, IrE];
```

```
In[34]:= GTCLCLebschGordanTable[IrE, IrA2, {cgk5}, {"E"}]
```

		E	
j	k	1	2
1	1	0	-1
2	1	1	0

Figure 7.12 Verify the transformation behavior of the perturbations $A_{0,x}x$, $A_{0,y}y$, and $A_{0,z}z$.

8

Generalization to Include the Spin

Es wird, namentlich im Hinblick auf den Millikan-Landéschen Befund der Darstellbarkeit der Alkalidubletts [...], die Auffassung vorgeschlagen, dass in diesen Dubletts und ihrem anomalen Zeemaneffekt eine klassisch nicht beschreibbare Zweideutigkeit der quantentheoretischen Eigenschaften des Leuchtelektrons zum Ausdruck kommt, [...].

Wolfgang Pauli

(*Zeitschrift für Physik*, 1, 31, 765–783 (1925))

The electron spin is an additional degree of freedom with a purely quantum mechanical origin. Spin-full systems can be effectively described by the PAULI equation which exhibits a similar form as the SCHRÖDINGER equation, but incorporates the coupling of the spin to a magnetic field, e.g., originating from the particles orbital motion. During the chapter the symmetry group of the PAULI equation is discussed which leads to the concept of double groups. Double groups naturally arise for spin 1/2 particles where a rotation of 4π represents the identity. This concept helps to discuss the splitting of electronic states under strong spin orbit coupling as it is present for systems containing heavy elements. The chapter closes with degeneracies occurring due to an additional time-reversal symmetry.

8.1

The PAULI Equation

In Chapter 7 the spin-independent SCHRÖDINGER equation was discussed. However, each electron carries a spin and an immanent magnetic moment. For a central-force potential the movement of the electrons can be seen as a current loop, inducing a magnetic field that couples to the spin magnetic moment of each electron. This leads to the spin–orbit coupling term

$$\hat{H}_{\text{SOC}} = -\frac{\hbar}{4m^2c^2r} \frac{\partial V(r)}{\partial r} \hat{\mathbf{s}} \cdot \hat{\mathbf{L}}, \quad (8.1)$$

where $\hat{\mathbf{L}} = \mathbf{r} \times \hat{\mathbf{p}}$ denotes the angular momentum operator and $\hat{\mathbf{s}}$ the spin operator. The components of the spin operator are given in terms of the PAULI matrices (2.70),

$$\hat{s}_i = \frac{\hbar}{2} \underline{\sigma}_i. \quad (8.2)$$

Adding the spin-orbit coupling to the SCHRÖDINGER equation and including the vector potential $\mathbf{A}$ describing the coupling to an electromagnetic field gives the so-called PAULI equation [116],

$$\left[\frac{(\hat{\mathbf{p}} - e\mathbf{A})^2}{2m} + V(r) - \frac{\hbar}{4m^2 c^2 r} \frac{\partial V(r)}{\partial r} \hat{\mathbf{s}} \cdot \hat{\mathbf{L}} \right] \Phi(\mathbf{r}) = E \Phi(\mathbf{r}). \quad (8.3)$$

The solutions of the PAULI equation are spinor functions of the form

$$\Phi = \begin{pmatrix} \phi_1(\mathbf{r}) \\ \phi_2(\mathbf{r}) \end{pmatrix}. \quad (8.4)$$

The PAULI-Hamiltonian is a linear operator acting on a HILBERT space $\mathcal{H}$ with $\Phi \in \mathcal{H}$. The inner product of $\mathcal{H}$ is defined via

$$(\Phi(\mathbf{r}), \Psi(\mathbf{r})) = \int d^3r [\phi_1(\mathbf{r})^* \psi_1(\mathbf{r}) + \phi_2(\mathbf{r})^* \psi_2(\mathbf{r})], \quad (8.5)$$

which implies that the components of the spinor function $\phi_\alpha(\mathbf{r})$ have to be square integrable functions, $\phi_\alpha \in L^2$. The spin-orbit coupling operator $\hat{H}_{\text{SOC}}$ of equation (8.1) contains the operators $\hat{L}_i$ and $\hat{s}_i$. The components of the angular momentum operator, for example,

$$\hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), \quad (8.6)$$

are differential operators acting on each component of Φ , meaning in the space L^2 , $\hat{L}_i: L^2 \rightarrow L^2$. According to equation (8.2), the components of the spin operator $\hat{s}_i$ are complex 2×2 -matrices acting on the HILBERT space $\mathbb{C}^2$, the space of the 2-dimensional vectors over the field of complex numbers. Hence, the solution of the PAULI equation Φ , is an eigenfunction of the PAULI-Hamiltonian with eigenvalue E and furthermore an element of the HILBERT space $\mathcal{H}$ which is a direct product space of L^2 and $\mathbb{C}^2$, $\mathcal{H} = L^2 \otimes \mathbb{C}^2$.

8.2

Homomorphism between $SU(2)$ and $SO(3)$

In the three-dimensional space, the rotation matrices of the group $SO(3)$ form a faithful representation of proper point groups. Rotations in spin-space, however, can be represented faithfully by matrices of the group $SU(2)$. It will be shown in the following that there are always two matrices of the group $SU(2)$ that can be mapped to one matrix of $SO(3)$.

Theorem 36 (Homomorphism between $SU(2)$ and $SO(3)$). *There exists a two-to-one homomorphism $\Pi : SU(2) \rightarrow SO(3)$ of the group $SU(2)$ onto $SO(3)$, with*

$$\underline{\underline{R}}(\underline{u}) = \underline{\underline{R}}(-\underline{u}) , \quad (8.7)$$

for each $\underline{u}, -\underline{u} \in SU(2)$ and $\underline{\underline{R}} \in SO(3)$.

Proof. Each position vector $\mathbf{r} \in \mathbb{R}^3$, with $\mathbf{r} = (x, y, z)$, can be mapped to a traceless matrix $\underline{\underline{m}}(\mathbf{r}) = \boldsymbol{\sigma} \cdot \mathbf{r}$,

$$\underline{\underline{m}}(\mathbf{r}) = \begin{pmatrix} z & x - iy \\ x + iy & -z \end{pmatrix} . \quad (8.8)$$

For each matrix $\underline{u} \in SU(2)$, $\underline{\underline{m}}(\mathbf{r})$ can be transformed to $\underline{\underline{m}}(\mathbf{r}')$, via

$$\underline{\underline{m}}(\mathbf{r}') = \underline{u} \underline{\underline{m}}(\mathbf{r}) \underline{u}^{-1} = \begin{pmatrix} z' & x' - iy' \\ x' + iy' & -z' \end{pmatrix} . \quad (8.9)$$

Since $\mathbf{r}$ and $\mathbf{r}'$ are both vectors of $\mathbb{R}^3$, a rotation matrix $\underline{\underline{R}}(\underline{u})$ can be found such that

$$\mathbf{r}' = \underline{\underline{R}}(\underline{u}) \cdot \mathbf{r} . \quad (8.10)$$

There are two things to proof. First, $\underline{\underline{R}}(\underline{u}) \in SO(3)$ and second, $\underline{\underline{R}}(\underline{u}) = \underline{\underline{R}}(-\underline{u})$.

1. To show that $\underline{\underline{R}}(\underline{u}) \in SO(3)$, it will first be verified that the transformation (8.10) preserves the scalar product and that $\det \underline{\underline{R}} = 1$. The scalar product of the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ can be written by means of (8.8) as

$$\mathbf{r}_1 \cdot \mathbf{r}_2 = \frac{1}{2} \text{Tr} (\underline{\underline{m}}(\mathbf{r}_1) \underline{\underline{m}}(\mathbf{r}_2)) . \quad (8.11)$$

Hence, one obtains

$$\begin{aligned} \mathbf{r}'_1 \cdot \mathbf{r}'_2 &= \frac{1}{2} \text{Tr} (\underline{u} \underline{\underline{m}}(\mathbf{r}_1) \underline{u}^{-1} \underline{u} \underline{\underline{m}}(\mathbf{r}_2) \underline{u}^{-1}) \\ &= \mathbf{r}_1 \cdot \mathbf{r}_2 . \end{aligned} \quad (8.12)$$

Since (8.10) preserves the scalar product, it follows that either $\det \underline{\underline{R}} = 1$ or $\det \underline{\underline{R}} = -1$. Furthermore, for $\mathbf{r} = \mathbf{r}'$ the determinant of the identity matrix is given by $\det \underline{\underline{R}} = 1$. It can be shown that $SU(2)$ is a connected Lie group and hence, $\det \underline{\underline{R}}(\underline{u})$ has to be a continuous function of $\underline{u}$. This gives $\det \underline{\underline{R}}(\underline{u}) = 1$ for every $\underline{u} \in SU(2)$.

2. To see that $\underline{\underline{R}}(\underline{u}) = \underline{\underline{R}}(-\underline{u})$ is obvious. Going back to equation (8.9) and replacing $\underline{u}$ by $-\underline{u}$ will give the same matrix $\underline{\underline{m}}(\mathbf{r}')$.

□

Theorem 37 (Explicit form of homomorphism between $SU(2)$ and $SO(3)$). *An explicit form of the two-to-one homomorphism $\Pi : SU(2) \rightarrow SO(3)$ of the group $SU(2)$ onto $SO(3)$ is given by*

$$R_{ij}(\underline{u}) = \frac{1}{2} \text{Tr} [\underline{\sigma}_i \underline{u} \underline{\sigma}_j \underline{u}^{-1}] , \quad (8.13)$$

where $\underline{u} \in SU(2)$ and $\underline{R} \in SO(3)$.

Proof. The theorem follows from equation (8.8) and equation (8.9) and writing

$$x' \underline{\sigma}_1 + y' \underline{\sigma}_2 + z' \underline{\sigma}_3 = x \underline{u} \underline{\sigma}_1 \underline{u}^{-1} + y \underline{u} \underline{\sigma}_2 \underline{u}^{-1} + z \underline{u} \underline{\sigma}_3 \underline{u}^{-1} . \quad (8.14)$$

Multiplying from the left with $\underline{\sigma}_i$, taking the trace and using the equality

$$\text{Tr} [\underline{\sigma}_i \underline{\sigma}_j] = 2\delta_{ij} \quad (8.15)$$

gives

$$x' = \frac{1}{2} (x \text{Tr} [\underline{\sigma}_1 \underline{u} \underline{\sigma}_1 \underline{u}^{-1}] + y \text{Tr} [\underline{\sigma}_1 \underline{u} \underline{\sigma}_2 \underline{u}^{-1}] + z \text{Tr} [\underline{\sigma}_1 \underline{u} \underline{\sigma}_3 \underline{u}^{-1}]) \quad (8.16)$$

$$= R_{11}x + R_{12}y + R_{13}z . \quad (8.17)$$

In a similar manner, equations for y' and z' follow by multiplying from the left with $\underline{\sigma}_2$ and $\underline{\sigma}_3$, respectively. $\square$

8.3

Transformation of the Spin–Orbit Coupling Operator

In the following, the transformation behavior of the spin–orbit coupling operator is discussed by investigating the transformation of the components of the angular momentum operator and the transformation of the spin operator separately [117].

According to Section 2.2.1, the coordinate transformation of an arbitrary scalar function $\phi : \mathbb{R}^3 \rightarrow \mathbb{C}$ can be written as

$$\hat{P}(T)^{-1} \phi(\mathbf{r}) = \phi(\underline{R}(T) \cdot \mathbf{r}) . \quad (8.18)$$

Defining the vector $\mathbf{r}'$ via $\mathbf{r}' = \underline{R}(T) \cdot \mathbf{r}$, the derivatives of the components r'_i with respect to r_j are given by the components of the rotation matrix,

$$\frac{\partial r'_i}{\partial r_j} = R_{ij}(T) . \quad (8.19)$$

Consequently, the derivative of the transformed function ϕ with respect to r_j can be calculated using the chain rule,

$$\frac{\partial}{\partial r_i} \phi(\mathbf{r}') = \sum_{j=1}^3 R_{ji} \frac{\partial}{\partial r'_j} \phi(\mathbf{r}') , \quad i = 1, \dots, 3 . \quad (8.20)$$

This result can be used to discuss the transformation behavior of the angular momentum operator.

Theorem 38 (Transformation of the angular momentum operator). *For a coordinate transformation $\hat{P}(T)$, the components $\hat{L}_i$ of the angular momentum operator transform as*

$$\hat{P}(T)\hat{L}_i\hat{P}(T)^{-1} = \det(\underline{\underline{R}}(T)) \sum_{j=1}^3 R_{ji}(T)\hat{L}_j. \quad (8.21)$$

Proof. It suffices to prove the theorem for

$$\hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right). \quad (8.22)$$

Using the relation for the inverse rotation matrix¹⁾

$$\underline{\underline{R}}(T)^{-1} = \det(\underline{\underline{R}}(T)) \underline{\underline{R}}(T)^T \quad (8.23)$$

together with equation (8.20), one can obtain

$$\hat{P}(T)\hat{L}_x\hat{P}(T)^{-1}\phi(\mathbf{r}) = -i\hbar\hat{P}(T) \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \phi(\underline{\underline{R}}(T) \cdot \mathbf{r}) \quad (8.24)$$

$$= -i\hbar \det(\underline{\underline{R}}(T)) \left[\left(\sum_{i=1}^3 R_{i2}r_i \right) \left(\sum_{j=1}^3 R_{j3} \frac{\partial \phi(\mathbf{r})}{\partial r_j} \right) - \left(\sum_{i=1}^3 R_{i3}r_i \right) \left(\sum_{j=1}^3 R_{j2} \frac{\partial \phi(\mathbf{r})}{\partial r_j} \right) \right] \quad (8.25)$$

$$= -i\hbar \det(\underline{\underline{R}}(T)) \sum_{i=1}^3 \sum_{j=1}^3 (R_{i2}R_{j3} - R_{i3}R_{j2}) r_i \frac{\partial \phi(\mathbf{r})}{\partial r_j}. \quad (8.26)$$

Using

$$\begin{vmatrix} R_{i2} & R_{i3} \\ R_{j2} & R_{j3} \end{vmatrix} = R_{i2}R_{j3} - R_{i3}R_{j2} \quad (8.27)$$

1) SO(3) matrices are orthogonal and thus $\underline{\underline{R}}(T)^{-1} = \underline{\underline{R}}(T)^T$. For O(3) matrices, the determinant is ± 1 . Hence, the inverse is given by $\underline{\underline{R}}(T)^{-1} = \det(\underline{\underline{R}}(T)) \underline{\underline{R}}(T)^T$.

and expanding the products in (8.26) gives

$$\begin{aligned}
 \hat{P}(T)\hat{L}_1\hat{P}(T)^{-1}\phi(\mathbf{r}) &= -i\hbar \det(\underline{R}(T)) \\
 &\times \left[\left(0 \cdot r_1 + \begin{vmatrix} R_{22} & R_{23} \\ R_{12} & R_{13} \end{vmatrix} \cdot r_2 + \begin{vmatrix} R_{32} & R_{33} \\ R_{12} & R_{13} \end{vmatrix} \cdot r_3 \right) \frac{\partial \phi(\mathbf{r})}{\partial r_1} \right. \\
 &+ \left(\begin{vmatrix} R_{12} & R_{13} \\ R_{22} & R_{23} \end{vmatrix} \cdot r_1 + 0 \cdot r_2 + \begin{vmatrix} R_{32} & R_{33} \\ R_{22} & R_{23} \end{vmatrix} \cdot r_3 \right) \frac{\partial \phi(\mathbf{r})}{\partial r_2} \\
 &\left. + \left(\begin{vmatrix} R_{12} & R_{13} \\ R_{32} & R_{33} \end{vmatrix} \cdot r_1 + \begin{vmatrix} R_{22} & R_{23} \\ R_{32} & R_{33} \end{vmatrix} \cdot r_2 + 0 \cdot r_3 \right) \frac{\partial \phi(\mathbf{r})}{\partial r_3} \right]. \quad (8.28)
 \end{aligned}$$

From the general equation of the inverse of a 3×3 -matrix [118] it is possible to find

$$\begin{aligned}
 \hat{P}(T)\hat{L}_1\hat{P}(T)^{-1}\phi(\mathbf{r}) &= -i\hbar \left[(R_{12}^{-1}r_3 - R_{13}^{-1}r_2) \frac{\partial \phi(\mathbf{r})}{\partial r_1} \right. \\
 &\left. + (R_{13}^{-1}r_1 - R_{11}^{-1}r_3) \frac{\partial \phi(\mathbf{r})}{\partial r_2} + (R_{11}^{-1}r_2 - R_{12}^{-1}r_3) \frac{\partial \phi(\mathbf{r})}{\partial r_3} \right]. \quad (8.29)
 \end{aligned}$$

Using the relation (8.23) for the inverse of a rotation matrix and rearranging afterwards will give equation (8.21). $\square$

As stated in Section 2.2.3, the spin is an axial vector, which is invariant under inversion. Hence, using the PAULI gauge the inversion in spin space is represented by the application of the identity matrix (2.82). Hence, the application of a transformation according to an improper rotation (inversion + proper rotation) has to equal the application of a transformation according to a proper rotation.

Theorem 39 (Transformation of the spin operator). *For a coordinate transformation in spin space $\underline{u}(T) \in SU(2)$ the transformation of a component of the spin operator $\hat{s}_i$ can be written as*

$$\underline{u}(T) \cdot \hat{s}_i \cdot \underline{u}(T)^{-1} = \det(\underline{R}(T)) \sum_{j=1}^3 R_{ji}(T) \hat{s}_j. \quad (8.30)$$

For a set of elements T , the transformation of the spin-orbit coupling operator is given by the composition of the transformation operators $\hat{P}$ and $\underline{u}$, $\hat{P} \otimes \underline{u}$. In Theorem 36, it was shown that there exists a two-to-one homomorphism Π from the group $SU(2)$ representing the transformations in spin space to the group of all proper rotations $SO(3)$. According to Theorems 38 and 39, the transformation of the components of the angular momentum operator and the spin operator are multiplied with the determinant of the rotation matrix. Hence, all transformations of the spin-orbit coupling operator are represented by proper rotations. The group $SU(2)$ is a faithful representation of all transformations of the spin-orbit coupling operator.

8.4

The Group of the PAULI Equation and Double Groups

Installation of double groups	
GTChangeRepresentation	Specifies the standard representation used by GTPack
GTWhichRepresentation	Gives the currently used standard representation
GOREpresentation	An option of GTInstallGroup for the specification of the standard representation

In correspondence to the symmetry of the SCHRÖDINGER equation it is necessary to distinguish between three different isomorphic groups, the abstract point group (now denoted by $\mathcal{G}_p$), its faithful matrix representation $\mathcal{G} \subset O(3)$ using three-dimensional rotation matrices, and the group of the SCHRÖDINGER equation $\mathcal{G}_{\text{SEQ}}$ containing all operators $\hat{P}$ that leave the SCHRÖDINGER equation invariant. The relationship is shown in Figure 8.1. Analogously to the group of the SCHRÖDINGER equation, the group of the PAULI equation $\bar{\mathcal{G}}_{\text{PEQ}}$ is the group of all transformations $\hat{P} \otimes \underline{u}$ that leave the PAULI equation invariant. Again, it is possible to imagine an abstract point group $\bar{\mathcal{G}}_p \simeq \bar{\mathcal{G}}_{\text{PEQ}}$ with elements $\bar{T} \in \bar{\mathcal{G}}_p$ ²⁾.

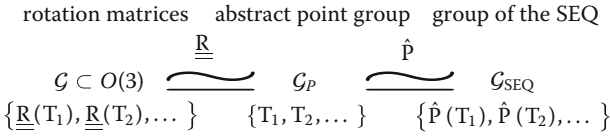


Figure 8.1 Isomorphism between an abstract point group $\mathcal{G}_p$, the faithful representation $\mathcal{G} \subset O(3)$, and the group of the SCHRÖDINGER equation $\mathcal{G}_{\text{SEQ}}$.

All elements $\bar{T} \in \bar{\mathcal{G}}_p$ have to fulfill the property $\hat{P}(\bar{T})V(\mathbf{r}) = V(\mathbf{r})$. Therefore, the number of elements in the group of the PAULI equation is restricted by the potential $V(\mathbf{r})$. Furthermore, there are twice as many elements in the group of the PAULI equation than in the group of the SCHRÖDINGER equation (Theorem 36), because there are always two elements $\bar{T}_1$ and $\bar{T}_2$ with the property $\Pi(\underline{u}(\bar{T}_1)) = \Pi(\underline{u}(\bar{T}_2))$. The group $\bar{\mathcal{G}}_p$ is called the **double group** of the point group $\mathcal{G}_p$.

For the implementation of a double group $\bar{\mathcal{G}}_p$ in GTPack it is necessary to find a faithful matrix representation. Following the definition of DAMHUS [117] this representation can be constructed as follows.

Definition 41 (Matrix representation of a double group). *Consider a point group $\mathcal{G}_p$ and its corresponding double group $\bar{\mathcal{G}}_p$. A faithful matrix representation $\bar{\mathcal{G}}$ of the abstract group $\bar{\mathcal{G}}_p$ can be found by distinguishing the following three cases.*

- 2) In the following, all groups that are isomorphic to a group of transformations of the form $\hat{P} \otimes \underline{u}$, i.e., double groups, are denoted with a bar.

Mathematica**GTChangeRepresentation, GTGroupFromGenerators**

To work with double groups, the standard representation has to be changed.
Using SU(2) it is possible to obtain rotation matrices in spin space.

```
In[9]:= GTChangeRepresentation["SU(2)"]
```

The standard representation has changed to SU(2)

Two generators of the group O are $C_{3\alpha}$ and C_{4x} .

```
In[10]:= GTGetMatrix[C3α] // MatrixForm
```

Out[10]//MatrixForm=

$$\begin{pmatrix} \frac{1}{2} + \frac{i}{2} & -\frac{1}{2} - \frac{i}{2} \\ \frac{1}{2} - \frac{i}{2} & \frac{1}{2} - \frac{i}{2} \end{pmatrix}$$

```
In[11]:= GTGetMatrix[C4x] // MatrixForm
```

Out[11]//MatrixForm=

$$\begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$$

Using GTGroupFromGenerators the double group of O is installed.

```
In[12]:= GTGroupFromGenerators[{C3α, C4x}]
```

$$\text{Out[12]} = \left\{ Ee, \bar{E}e, \bar{C}_{3\delta}, \bar{C}_{3\gamma}^{-1}, \bar{C}_{3\alpha}, \bar{C}_{3\beta}^{-1}, \bar{C}_{3\beta}, \bar{C}_{3\gamma}, \bar{C}_{3\delta}^{-1}, C_{2y}, C_{2x}, \bar{C}_{2x}, \bar{C}_{2y}, C_{2a}, \bar{C}_{2b}, C_{2b}, \bar{C}_{2a}, C_{2z}, \bar{C}_{2z}, C_{2e}, C_{2c}, C_{2d}, \bar{C}_{2f}, C_{2f}, \bar{C}_{2d}, \bar{C}_{2c}, \bar{C}_{2e}, C_{3\delta}^{-1}, C_{3\gamma}, C_{3\beta}, C_{3\alpha}^{-1}, C_{3\alpha}, C_{3\beta}^{-1}, C_{3\gamma}, C_{3\delta}, \bar{C}_{4x}, \bar{C}_{4y}^{-1}, \bar{C}_{4z}, \bar{C}_{4x}^{-1}, \bar{C}_{4y}, \bar{C}_{4z}^{-1}, C_{4y}, C_{4x}, C_{4z}, C_{4y}^{-1}, C_{4x}^{-1}, C_{4z}^{-1} \right\}$$

Double groups containing the inversion need the representation SU(2)xS.

```
In[13]:= GTChangeRepresentation["SU(2)xS"]
```

The standard representation has changed to SU(2)xS.

```
In[14]:= GTGetMatrix[IEe] // MatrixForm
```

Out[14]//MatrixForm=

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Including the inversion, the double group of O_h is obtained.

```
In[15]:= GTGroupFromGenerators[{IEe, C3α, C4x}]
```

$$\text{Out[15]} = \left\{ Ee, \bar{E}e, \bar{C}_{3\delta}, \bar{C}_{3\gamma}^{-1}, \bar{C}_{3\alpha}, \bar{C}_{3\beta}^{-1}, \bar{C}_{3\beta}, \bar{C}_{3\gamma}, \bar{C}_{3\delta}^{-1}, C_{2y}, C_{2x}, \bar{C}_{2x}, \bar{C}_{2y}, C_{2a}, \bar{C}_{2b}, C_{2b}, \bar{C}_{2a}, C_{2z}, \bar{C}_{2z}, C_{2e}, C_{2c}, C_{2d}, \bar{C}_{2f}, C_{2f}, \bar{C}_{2d}, \bar{C}_{2c}, \bar{C}_{2e}, C_{3\delta}^{-1}, C_{3\gamma}, C_{3\beta}, C_{3\alpha}^{-1}, C_{3\alpha}, C_{3\beta}^{-1}, C_{3\gamma}, C_{3\delta}, \bar{C}_{4x}, \bar{C}_{4y}^{-1}, \bar{C}_{4z}, \bar{C}_{4x}^{-1}, \bar{C}_{4y}, \bar{C}_{4z}^{-1}, C_{4y}, C_{4x}, C_{4z}, \bar{IE}e, IEe, IC_{2y}, IC_{2x}, \bar{IC}_{2x}, \bar{IC}_{2y}, IC_{2a}, \bar{IC}_{2b}, IC_{2b}, \bar{IC}_{2a}, IC_{2z}, \bar{IC}_{2z}, IC_{2e}, IC_{2c}, IC_{2d}, \bar{IC}_{2f}, IC_{2f}, \bar{IC}_{2d}, \bar{IC}_{2c}, \bar{IC}_{2e}, \bar{IC}_{3\delta}, \bar{IC}_{3\gamma}^{-1}, \bar{IC}_{3\beta}, \bar{IC}_{3\alpha}^{-1}, \bar{IC}_{3\alpha}, \bar{IC}_{3\beta}, \bar{IC}_{3\gamma}, \bar{IC}_{3\delta}^{-1}, IC_{3\delta}, IC_{3\gamma}, IC_{3\beta}, IC_{3\alpha}^{-1}, IC_{3\alpha}, IC_{3\beta}^{-1}, IC_{3\gamma}, IC_{3\delta}, \bar{IC}_{4x}, \bar{IC}_{4y}^{-1}, \bar{IC}_{4z}, \bar{IC}_{4x}^{-1}, \bar{IC}_{4y}, \bar{IC}_{4z}^{-1}, IC_{4y}, IC_{4x}, IC_{4z}, IC_{4y}^{-1}, IC_{4x}^{-1}, IC_{4z}^{-1} \right\}$$

Figure 8.2 Installation of the double group of O and O_h using GTGroupFromGenerators.

1. $\mathcal{G}_p$ is a proper point group. $\bar{\mathcal{G}}$ is given by all $SU(2)$ matrices that can be associated to an element $T \in \mathcal{G}_p$ by applying the homomorphism Π (see Theorem 36),

$$\bar{\mathcal{G}} = \{ \underline{u} \in SU(2) : \Pi(\underline{u}) = \underline{R}(T), T \in \mathcal{G}_p \}. \quad (8.31)$$

2. $\mathcal{G}_p$ is a point group containing the inversion $I \in \mathcal{G}_p$. Construct the proper point group $\mathcal{G}_0 = \{ T \in \mathcal{G} : \det(\underline{R}(T)) = 1 \}$ and the group $S = \{ 1, -1 \}$. According to case 1) it is possible to generate the group $\bar{\mathcal{G}}_0 \in SU(2)$. $\bar{\mathcal{G}}$ is given by the direct product $\bar{\mathcal{G}}_0 \times S$ (see Definition 17),

$$\bar{\mathcal{G}} = \bar{\mathcal{G}}_0 \times S. \quad (8.32)$$

3. $\mathcal{G}_p$ is an improper point group without inversion $I \notin \mathcal{G}_p$. Construct a group of proper rotation matrices according to $\mathcal{G}' = \{ \det(\underline{R}(T)) \underline{R}(T), T \in \mathcal{G} \}$. ($\mathcal{G}'$ is isomorphic to $\mathcal{G}_p$). $\bar{\mathcal{G}}$ is constructed from $\mathcal{G}'$ according to case 1),

$$\bar{\mathcal{G}} = \{ \underline{u} \in SU(2) : \Pi(\underline{u}) = \underline{R}', \forall \underline{R}' \in \mathcal{G}' \}. \quad (8.33)$$

The following examples will show the installation of double groups in GTPack.

Example 45 (Changing the standard representation). According to Definition 41, double groups of proper point groups can be represented by $SU(2)$ rotation matrices. For each symbol, an associated $SU(2)$ matrix is implemented in GTPack. GTPack has an internal variable `grpgrp`, which specifies the standard representation to decide whether **GTGetMatrix** gives an ordinary rotation matrix of $O(3)$ or a matrix of the group $SU(2)$. This internal variable can be changed using the command **GTChangeRepresentation**, as can be seen in Figure 8.2. Using the elements C_{3x} and C_{4x} it is possible to generate the double group of the cubic point group O . According to Definition 41, pure $SU(2)$ matrices can not be taken if the point group contains the inversion operation. In this case, matrices of the direct product $SU(2) \times S$, $S = \{ -1, 1 \}$ should be used. This representation can be applied by specifying `GTChangeRepresentation["SU(2)xS"]`.

Example 46 (Installation of double groups in GTPack). In a second example **GTInstallGroup** will be used for the installation of double groups. By specifying the option **GOREpresentation** it can be chosen which standard representation should be used by GTPack. In Figure 8.3, the installation of the double groups of O and O_h is illustrated.

Mathematica**GTChangeRepresentation, GTGetMatrix, GTGroupFromGenerators**

To install a double group using GTInstallGroup the option *GOREpresentation* → "SU(2)" is specified.

```
In[9]:= GTInstallGroup[O, GOREpresentation → "SU(2)"]
```

The standard representation has changed to SU(2)

```
Out[9]:= {Ee, Ee, C̄3α, C̄3γ-1, C̄3β-1, C̄3α, C̄3β-1, C̄3γ, C̄3α-1, C̄3β, C̄3γ-1, C2y, C2x, C̄2x, C̄2y, C2a, C̄2b,  
C2b, C̄2a, C2z, C̄2z, C2e, C2c, C̄2d, C̄2f, C̄2d, C̄2c, C̄2e, C̄3α-1, C̄3γ, C̄3β, C̄3α-1,  
C̄3α, C̄3β-1, C̄3γ-1, C̄3α, C̄4y, C̄4x, C̄4x-1, C̄4y, C̄4z, C̄4z-1, C̄4y, C̄4x, C̄4y-1, C̄4z}
```

Similarly *GOREpresentation* → "SU(2)xS" is used for groups having the inversion as a symmetry element.

```
In[10]:= GTInstallGroup[Oh, GOREpresentation → "SU(2)xS"]
```

The standard representation has changed to SU(2)xS

```
Out[10]:= {Ee, Ee, C̄3α, C̄3γ-1, C̄3β-1, C̄3α, C̄3β-1, C̄3γ, C̄3α-1, C̄3β, C̄3γ-1, C2y, C2x, C̄2x, C̄2y, C2a, C̄2b, C2b, C̄2a, C2z,  
C̄2z, C2e, C2c, C̄2d, C̄2f, C̄2d, C̄2c, C̄2e, C̄3α-1, C̄3γ, C̄3β, C̄3α-1, C̄3γ, C̄3β, C̄3α-1, C̄3γ, C̄3β, C̄4y,  
C̄4x, C̄4x-1, C̄4y, C̄4z, C̄4z-1, C̄4y, C̄4x, C̄4y-1, C̄4z, I Ee, I Ee, I C2y, I C2x, I C̄2x, I C̄2y,  
I C2a, I C̄2b, I C̄2b, I C̄2a, I C̄2z, I C̄2z, I C̄2e, I C̄2c, I C̄2d, I C̄2f, I C̄2d, I C̄2c, I C̄2e,  
I C̄3α-1, I C̄3γ, I C̄3β-1, I C̄3α, I C̄3β-1, I C̄3γ, I C̄3α-1, I C̄3β, I C̄3γ-1, I C̄3α, I C̄3β-1, I C̄3γ,  
I C̄3α-1, I C̄3β, I C̄4y, I C̄4x, I C̄4x-1, I C̄4y, I C̄4z, I C̄4z-1, I C̄4y, I C̄4x, I C̄4y-1, I C̄4z}
```

Figure 8.3 Installation of the double group of O and O_h using GTInstallGroup.

8.5

Irreducible Representations of Double Groups

In the following, irreducible representations of double groups will be discussed and the connection to irreducible representations of proper point groups will be established. Since there are always two matrices $\pm \underline{u} \in SU(2)$ that can be mapped to a rotation matrix in $SO(3)$, each proper rotation T has a partner $\bar{T}$ within double groups. The same holds for the identity element E , which can be understood as a rotation about 2π for ordinary groups. For a double group, the identity element E represents a rotation about 4π , whereas the rotation about 2π gives the element $\bar{E}$. In the following, the elements of a double group $\bar{\mathcal{G}}$ are identified by either T or $\bar{T} = \bar{E} \cdot T$, where T has to be understood as an element of the ordinary point group $\mathcal{G}$. The connection between the classes of the ordinary point group $\mathcal{G}$ and the classes of the associated double group $\bar{\mathcal{G}}$ is summarized in the theorem of OPECHOWSKI [119].³⁾

Theorem 40 (Theorem of OPECHOWSKI). *Given a point group $\mathcal{G}$, a class $C \subset \mathcal{G}$, and the associated double group $\bar{\mathcal{G}}$. For the classes $\bar{C} \subset \bar{\mathcal{G}}$ one of the following cases will be true.*

1. *The elements $T \in C$ are either noncommuting or coaxial $\Rightarrow$ there are two distinct classes $\bar{C}(T)$ and $\bar{C}(\bar{T})$ for the double group $\bar{\mathcal{G}}$.*

3) A proof can be found e.g., in the book by ALTMANN [38].

2. The elements $T \in C$ are binary rotations with perpendicular rotation axes $\Rightarrow$ the classes $\overline{C}(T)$ and $\overline{C}(\overline{T})$ are identical.

From the theorem of OPECHOWSKI it follows that the number of classes $\overline{N}$ in a double group $\overline{G}$ is higher in comparison to the number of classes N in an ordinary point group G (but not twice as high). Interestingly, all irreducible representations of G are also irreducible representations of $\overline{G}$. Since the number of classes equals the number of irreducible representations, $(\overline{N} - N)$ so-called extra-representations can be identified.

Theorem 41 (Irreducible representations of double groups). *Consider a group G with irreducible representations Γ^p and the associated double group $\overline{G}$ with irreducible representations $\overline{\Gamma}^q$. The following statements are true,*

1. Let $\overline{l}_q$ be the dimension of the irreducible representation $\overline{\Gamma}^q$. The representation matrix of $\overline{E}$ is either $+\underline{1}_{\overline{l}_q}$ or $-\underline{1}_{\overline{l}_q}$, where $\underline{1}_{\overline{l}_q}$ is the $\overline{l}_q$ -dimensional identity matrix.
2. Every irreducible representation Γ^p of G is also an irreducible representation of $\overline{G}$.
3. For every irreducible representation $\overline{\Gamma}^q$ of $\overline{G}$ that is not an irreducible representation of G it holds $\chi^q(\overline{E} \cdot T) = -\chi^q(T)$.

Proof.

1. The element $\overline{E}$ commutes with every element of $\overline{G}$. Since every irreducible representation of $\overline{G}$ is connected with $\overline{G}$ via a homomorphism, the same holds for the representation matrices. According to the first lemma of SCHUR (Theorem 14), a matrix that commutes with every matrix of an irreducible representation has to be a constant matrix $\lambda \underline{1}$. Furthermore, $\overline{E} \cdot \overline{E} = E$ and thus $\lambda \underline{1} \cdot \lambda \underline{1} = \lambda^2 \underline{1} = \underline{1}$, which gives $\lambda = \pm 1$.
2. Starting from the elements $T_1 \dots T_N \in G$, we can construct the group $\overline{G}$ via $\overline{G} = \{T_1 \dots T_N, \overline{E} \cdot T_1 \dots \overline{E} \cdot T_N\}$. Taking an irreducible representation Γ^p of G and defining $\underline{\Gamma}^p(\overline{E}) = \underline{1}_{l_p}$ it follows that Γ^p is a representation of $\overline{G}$. Furthermore, Γ^p is irreducible.
3. Constructing $\overline{G}$ as before and using the convention $\underline{\Gamma}^q(\overline{E}) = -\underline{1}_{\overline{l}_p}$ it can be verified that $\underline{\Gamma}^q(T) = -\underline{\Gamma}^q(\overline{E} \cdot T)$ and hence $\chi^q(\overline{E} \cdot T) = -\chi^q(T)$. $\square$

Example 47 (Classes of the double group $\overline{O}_h$). As an example the character table of the double group $\overline{O}_h$ is calculated. As usual the point group is installed using **GTInstallGroup**. The character table is computed using **GTCharacterTable**. The corresponding *Mathematica* code is illustrated in Figure 8.4. With the help of the character table it is possible to discuss the two theorems stated within this section. Starting with the theorem of OPECHOWSKI (Theorem 40), the following pairs of classes can be identified: $C_1 \leftrightarrow C_{15}$, $C_4 \leftrightarrow C_6$, $C_5 \leftrightarrow C_7$, $C_8 \leftrightarrow C_{10}$, $C_9 \leftrightarrow C_{11}$

Mathematica

GTInstallGroup, GTCharacterTable

Install the double group of the point group O_h .

```
In[9]:= DOh = GTInstallGroup[Oh, GOREpresentation -> "SU(2)xS"]
```

The standard representation has changed to $SU(2) \times S$

[illegible]

The character table of the double group is obtained using `GTCharacterTable`.

```
In[10]:= GTCharacterTable[DOh];
```

	6	6	6	6	6	8	8	8	12	12	12	12	12	12	12	12	12	12
	IC _{2y}	IC _{2y}	IC _{4y}	IC _{4y}	IC _{7y}	IC _{7y}	IC ₃₆	IC ₃₆	IC ₃₆	IC ₃₆	IC ₂₄	IC ₂₄	IC ₂₄	IC ₂₄	IC ₂₄	IC ₂₄	IC ₂₄	IC ₂₄
r ¹	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
r ²	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
r ³	1	-1	1	1	-1	1	-1	-1	1	-1	1	1	-1	-1	1	-1	1	-1
r ⁴	1	1	1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	1	1	1	1
r ⁵	2	-2	2	0	0	0	0	1	-1	1	-1	0	0	0	-2	2	-2	2
r ⁶	2	0	0	-√2	-√2	√2	√2	-1	-1	1	1	0	0	0	-2	-2	2	2
r ⁷	2	0	0	-√2	√2	√2	√2	1	-1	-1	1	0	0	0	2	-2	-2	-2
r ⁸	2	0	0	√2	-√2	-√2	-√2	1	-1	-1	1	0	0	0	2	-2	-2	-2
r ⁹	2	0	0	√2	√2	-√2	-√2	-1	-1	1	1	0	0	0	-2	-2	2	2
r ¹⁰	2	2	2	0	0	0	0	-1	-1	-1	-1	0	0	0	2	2	2	2
r ¹¹	3	-1	-1	-1	-1	-1	-1	0	0	0	0	1	1	3	3	3	3	3
r ¹²	3	-1	-1	1	1	1	1	0	0	0	0	0	-1	-1	3	3	3	3
r ¹³	3	1	-1	-1	-1	-1	-1	0	0	0	0	1	-1	-3	3	-3	-3	-3
r ¹⁴	3	1	-1	1	-1	1	-1	0	0	0	0	-1	1	-3	3	-3	-3	-3
r ¹⁵	4	0	0	0	0	0	0	-1	1	1	-1	0	0	0	-4	-4	-4	-4
r ¹⁶	4	0	0	0	0	0	0	1	1	-1	-1	0	0	0	-4	-4	-4	-4

$$C_1 = \{Ee\}$$

$$C_2 = \{IC_{2y}, IC_{2x}, \overline{IC}_{2x}, \overline{IC}_{2y}, IC_{2z}, \overline{IC}_{2z}\}$$

$$C_3 = \{C_{2y}, C_{2x}, \bar{C}_{2x}, \bar{C}_{2y}, C_{2z}, \bar{C}_{2z}\}$$

$$C_4 = \{\overline{IC}_{4y}, \overline{IC}_{4x}, \overline{IC}_{4x}^{-1}, \overline{IC}_{4y}^{-1}, \overline{IC}_{4z}, \overline{IC}_{4z}^{-1}\}$$

$$C_5 = \{\bar{C}_{4y}, \bar{C}_{4x}, \bar{C}_{4x}^{-1}, \bar{C}_{4y}^{-1}, \bar{C}_{4z}, \bar{C}_{4z}^{-1}\}$$

$$C_6 = \{IC_{4y}^{-1}, IC_{4x}^{-1}, IC_{4x}, IC_{4y}, IC_{4z}^{-1}, IC_{4z}\}$$

$$C_7 = \{C_{4y}^{-1}, C_{4x}^{-1}, C_{4x}, C_{4y}, C_{4z}^{-1}, C_{4z}\}$$

$$C_8 = \{\overline{IC}_{3\delta}, \overline{IC}_{3\gamma}^{-1}, \overline{IC}_{3\beta}^{-1}, \overline{IC}_{3\alpha}, \overline{IC}_{3\alpha}^{-1}, \overline{IC}_{3\beta}, \overline{IC}_{3\gamma}, \overline{IC}_{3\delta}^{-1}\}$$

$$C_9 = \{\bar{C}_{3\delta}, \bar{C}_{3Y}^{-1}, \bar{C}_{3\delta}^{-1}, \bar{C}_{3\alpha}, \bar{C}_{3\alpha}^{-1}, \bar{C}_{3\beta}, \bar{C}_{3Y}, \bar{C}_{3\delta}^{-1}\}$$

$$C_{10} = \{IC_{3\delta}^{-1}, IC_{3\gamma}, IC_{3\beta}, IC_{3\alpha}^{-1}, IC_{3\alpha}, IC_{3\delta}^{-1}, IC_{3\gamma}^{-1}, IC_{3\beta}\}$$

$$C_{11} = \{C_{35}^{-1}, C_{3\gamma}, C_{3\beta}, C_{3\alpha}^{-1}, C_{3\alpha}, C_{3\beta}^{-1}, C_{3\gamma}^{-1}, C_{35}\}$$

$$C_{12} = \{IC_{2a}, \overline{IC}_{2b}, IC_{2b}, \overline{IC}_{2a}, IC_{2c}, IC_{2c}, \overline{IC}_{2d}, \overline{IC}_{2e}, IC_{2e}, \overline{IC}_{2d}, \overline{IC}_{2c}, \overline{IC}_{2c}\}$$

$$C_{13} = \{C_{2a}, \bar{C}_{2b}, C_{2b}, \bar{C}_{2a}, C_{2c}, C_{2c}, C_{2d}, \bar{C}_{2e}, C_{2e}, \bar{C}_{2d}, \bar{C}_{2c}, \bar{C}_{2a}\}$$

$$C_{14} = \{\overline{IEe}\}$$

$$C_{1E} = \{\overline{E}\}$$

$$C_{16} = \{IEe\}$$

Figure 8.4 The character table of the double group $\overline{O}_h$.

and $C_{16} \leftrightarrow C_{14}$. All of them consist of elements either $T_1, \dots, T_N$ or $\overline{T}_1, \dots, \overline{T}_N$. The classes C_2, C_3, C_{12} , and C_{13} are mixed classes and contain both T and $\overline{T}$. C_3 and C_{13} contain binary rotations where the rotation axes are perpendicular to each other. C_2 and C_{12} contain reflections made up from the inversion and again a binary rotation with rotation axes perpendicular to each other. To identify the extra-representations one can pick, e.g., the character of the class $C_{15} = \{\overline{E}\}$. The irreducible representations $\Gamma^1, \Gamma^2, \Gamma^3, \Gamma^4, \Gamma^5, \Gamma^{10}, \Gamma^{11}, \Gamma^{12}, \Gamma^{13}$, and Γ^{14} have a character $\chi(\overline{E}) > 0$ and hence are also representations of the ordinary point group O_h . Since O_h has 10 irreducible representations and $\overline{O}_h$ has 16 classes, 6 extra-representations can be found ($\Gamma^6, \Gamma^7, \Gamma^8, \Gamma^9, \Gamma^{15}$, and Γ^{16}).

8.6

Splitting of Degeneracies by Spin–Orbit Coupling

Spin-orbit coupling	
GTSpinCharacters	Calculates the character system of the spin representation
GTSOCSplitting	Calculates the splitting of ordinary electronic states due to spin–orbit coupling

In the case of the SCHRÖDINGER equation, where the spin is not included intrinsically, an additional two-fold degeneracy due to the spin has to be taken into account for each energy level. In Example 40, it was shown that the 5-fold degenerate d -level splits into the 2-fold degenerate state E_g and the 3-fold degenerate state T_{2g} within a cubic crystal field. Including the spin degeneracy, the atomic d -state is 10-fold degenerate and the degeneracy of the states E_g and T_{2g} is 4 and 6, respectively. Since there is no 6-dimensional irreducible representation for the double group $\overline{O}_h$ an additional splitting has to occur, as soon as spin–orbit coupling is taken into account.

A matrix of the group $SU(2)$ is an operator in spin-space that transforms a spinor. For ordinary rotations, two matrices $+\underline{u}$ and $-\underline{u}$ can be constructed from equation (2.81). According to the PAULI gauge the inversion can be represented by the two-dimensional unit matrix $\underline{1}_2$ and hence also matrices for improper rotations can be constructed. However, referring to Definition 41, this matrix representation is not faithful in general.

According to Theorem 41, each irreducible representation Γ^p of an ordinary point group $\mathcal{G}$ is also an irreducible representation of the double group $\overline{\mathcal{G}}$. Choosing a set of basis functions $\phi_1^p, \dots, \phi_{l_p}^p$ of Γ^p of the ordinary point group $\mathcal{G}$ (which are scalar functions), it is possible to construct the $2 \times l_p$ -dimensional basis

$\Phi_1^{p,1}, \dots, \Phi_{l_p}^{p,1}, \Phi_1^{p,2}, \dots, \Phi_{l_p}^{p,2}$, using

$$\Phi_i^{p,1}(\mathbf{r}) = \begin{pmatrix} \phi_i^p(\mathbf{r}) \\ 0 \end{pmatrix} \quad \text{and} \quad \Phi_i^{p,2}(\mathbf{r}) = \begin{pmatrix} 0 \\ \phi_i^p(\mathbf{r}) \end{pmatrix}. \quad (8.34)$$

A transformation of such a spinor wave function by applying $\bar{\hat{P}}(T) = (\hat{P} \otimes \underline{\mathbb{1}})(T)$ gives

$$\bar{\hat{P}}(T) \Phi_{i,\beta}^{p,\alpha} = \sum_{\gamma=1}^2 u_{\gamma\beta}(T) \hat{P}(T) \Phi_{i,\gamma}^{p,\alpha} = \sum_{\gamma=1}^2 \sum_{j=1}^{l_p} u(T)_{\gamma\beta} \Gamma(T)_{ji} \Phi_{j,\gamma}^{p,\alpha}. \quad (8.35)$$

Hence, $\Phi_{i,\beta}^{p,\alpha}$ is a function belonging to the space of the direct product representation $\Gamma^p \otimes u$, which is a representation of the double group $\bar{\mathcal{G}}$. However, $\Gamma^p \otimes u$ is reducible in general and can be decomposed as follows,

$$\Gamma^p \otimes u = n_1 \bar{\Gamma}^1 \oplus n_2 \bar{\Gamma}^2 \oplus \dots \oplus n_{l_p} \bar{\Gamma}^{l_p}. \quad (8.36)$$

Applying Theorem 21, the number of times an irreducible representation $\bar{\Gamma}^q$ of the double group $\bar{\mathcal{G}}$ occurs in $\Gamma^p \otimes u$ can be calculated via

$$n_q = \frac{1}{g} \sum_{T \in \bar{\mathcal{G}}} [\bar{\chi}^q(T)]^* \chi^p(T) \chi^{1/2}(T), \quad (8.37)$$

where the abbreviation

$$\chi^{1/2}(T) = \text{Tr}(\underline{\mathbb{1}}(T)) \quad (8.38)$$

is used. The characters of the spin matrices $\chi^{1/2}$ can be calculated within GTPack by using **GTSpinCharacters**.

Example 48 (Spin characters and spin–orbit coupling). It was shown in Example 41 that the atomic d -states split into the states T_2 and E for a tetrahedral crystal field. By taking into account the spin degeneracy, the 6-fold degenerate state T_2 has to split as soon as spin–orbit coupling is taken into account. By calculating the character table for the double group $\bar{T}_d$ with GTPack, the level T_2 can be identified to be the representation Γ^6 (see Figure 8.5). To calculate the direct product $\Gamma^6 \otimes u$, the commands **GTSpinCharacters** and **GTDirectProductChars** can be used. **GTSpinCharacters** calculates the characters of the spin representation u . The splitting into irreducible representations of the double group $\bar{T}_d$ can be computed by using **GTlrep**,

$$\Gamma^6 \otimes u = \Gamma^4 \oplus \Gamma^8. \quad (8.39)$$

Mathematica

GTSpinCharacters

At first, the double group of T_d has to be installed. The information about the irreps of T_d can be found in the character table.

```
In[9]:= grp = GTInstallGroup[Td, GOREpresentation -> "SU(2)xS"];
```

```
ct = {classes, chars, names} = GTCharacterTable[grp];
```

The standard representation has changed to $SU(2) \times S$

	Ee	6 C _{2y}	6 IC _{4y}	6 IC _{4y} ⁻¹	8 C _{3z}	8 C _{3z} ⁻¹	12 IC _{2x}	Ee
Γ^1	1	1	1	1	1	1	1	1
Γ^2	1	1	-1	-1	1	1	-1	1
Γ^3	2	0	$-\sqrt{2}$	$\sqrt{2}$	-1	1	0	-2
Γ^4	2	0	$\sqrt{2}$	$-\sqrt{2}$	-1	1	0	-2
Γ^5	2	2	0	0	-1	-1	0	2
Γ^6	3	-1	-1	-1	0	0	1	3
Γ^7	3	-1	1	1	0	0	-1	3
Γ^8	4	0	0	0	1	-1	0	-4

$C_1 = \{Ee\}$

$C_2 = \{C_{2y}, C_{2x}, \bar{C}_{2x}, \bar{C}_{2y}, C_{2z}, \bar{C}_{2z}\}$

$C_3 = \{\bar{I}C_{4y}, \bar{I}C_{4x}, \bar{I}C_{4x}^{-1}, \bar{I}C_{4y}^{-1}, \bar{I}C_{4x}, \bar{I}C_{4x}^{-1}\}$

$C_4 = \{IC_{4y}^{-1}, IC_{4x}^{-1}, IC_{4x}, IC_{4y}, IC_{4x}^{-1}, IC_{4x}\}$

$C_5 = \{\bar{C}_{3z}, \bar{C}_{3y}^{-1}, \bar{C}_{3z}^{-1}, \bar{C}_{3x}, \bar{C}_{3x}^{-1}, \bar{C}_{3z}, \bar{C}_{3y}, \bar{C}_{3z}^{-1}\}$

$C_6 = \{C_{3z}^{-1}, C_{3y}, C_{3z}, C_{3x}^{-1}, C_{3x}, C_{3z}^{-1}, C_{3y}, C_{3z}\}$

$C_7 = \{IC_{2x}, \bar{I}C_{2y}, IC_{2y}, \bar{I}C_{2x}, IC_{2z}, IC_{2z}, \bar{I}C_{2x}, IC_{2y}, \bar{I}C_{2y}, \bar{I}C_{2z}, \bar{I}C_{2z}\}$

$C_8 = \{Ee\}$

The characters of the spin representation are calculated using GTSpinCharacters.

```
In[11]:= spinchars = GTSpinCharacters[classes]
```

```
Out[11]= {2, 0, -\sqrt{2}, \sqrt{2}, -1, 1, 0, -2}
```

By taking the direct product, the splitting of a T_2 level (Γ^6) can be verified.

```
In[12]:= dpchars = GTDirectProductChars[spinchars, chars[[6]]]
```

```
Out[12]= {6, 0, \sqrt{2}, -\sqrt{2}, 0, 0, 0, -6}
```

```
In[13]:= GTIrep[dpchars, ct]
```

$\Gamma^4 \oplus \Gamma^8$

```
Out[13]= {0, 0, 0, 1, 0, 0, 0, 1}
```

Figure 8.5 Application of GTSpinCharacters and GTIrep to estimate the splitting of the T_2 state due to spin–orbit coupling.

Example 49 (Spin-orbit coupling and tetrahedral symmetry). In the previous example, the influence of spin–orbit coupling to electrons in the state T_2 for tetrahedral symmetry was discussed. By applying **GTSOCSplitting**, the influence of spin–orbit coupling to all ordinary irreducible representations of a point group can be verified. After calculating the character table of a double group, **GTSOCSplitting** separates the ordinary irreducible representations from the extra-representations. Afterwards, the direct product $\Gamma^p \otimes u$ of an ordi-

Mathematica GTSOCSplitting

At first, the double group of T_d has to be installed and the character table has to be calculated.

```
In[9]:= grp = GTInstallGroup[Td, GOREpresentation -> "SU(2)xS"];
ct = GTCharacterTable[grp, GOverbose -> False, GOFast -> True];
```

The standard representation has changed to $SU(2) \times S$

GTSOCSplitting calculates the splitting of ordinary irreducible representations into extra-representations.

```
In[11]:= GTSOCSplitting[ct]
```

ord. irred. representations	Ee	C _{2y}	IC _{4y}	IC _{4y} ⁻¹	C _{3z}	C _{3z} ⁻¹	IC _{2x}	Ee	Spin-orbit coupling
Γ^1	1	1	1	1	1	1	1	1	Γ^1
Γ^2	1	1	-1	-1	1	1	-1	1	Γ^4
Γ^3	2	2	0	0	-1	-1	0	2	Γ^5
Γ^6	3	-1	-1	-1	0	0	1	3	$\Gamma^4 \oplus \Gamma^5$
Γ^7	3	-1	1	1	0	0	-1	3	$\Gamma^3 \oplus \Gamma^5$

extra-representations	Ee	C _{2y}	IC _{4y}	IC _{4y} ⁻¹	C _{3z}	C _{3z} ⁻¹	IC _{2x}	Ee
Γ^3	2	0	$-\sqrt{2}$	$\sqrt{2}$	-1	1	0	-2
Γ^4	2	0	$\sqrt{2}$	$-\sqrt{2}$	-1	1	0	-2
Γ^5	4	0	0	0	1	-1	0	-4

Figure 8.6 Application of GTSOCSplitting to calculate the influence of spin-orbit coupling to states with cubic symmetry.

nary irreducible representation Γ^p with the spin representation u is calculated according to (8.35). With the help of equation (8.37), $\Gamma^p \otimes u$ is decomposed into a CLEBSCH–GORDAN sum of extra-representations. Figure 8.6 illustrates the application of GTSOCSplitting to the double group T_d .

Task 27 (Crystal field splitting with spin). In Task 25 the splitting of d -levels was analyzed. Now the spin is taken into account. An octahedral complex is distorted tetragonally. Investigate the splitting of the levels.

1. Investigate the level splitting without spin first. Find the corresponding basis functions.
2. Investigate the level splitting due to spin-orbit interaction in an octahedral environment. Try to find basis spinors of the relevant irreducible representations (use a guess or proof results from literature).
3. The symmetry is lowered by the tetragonal distortion. Which additional splitting occurs, if spin is included?

Task 28 (Transformation behavior of spinors). The symmetry group D_3 is given. Analyze the transformation behavior of p -orbitals with respect to this group. Construct basis functions to the irreducible representations of D_3 starting from the p -orbitals. Include the spin, i.e., construct spinors from the p -orbitals and investigate the transformation behavior under the double group $\bar{D}_3$.

8.7

Time-Reversal Symmetry

Time-reversal symmetry	
GTReality	Estimates whether a representation is potentially real, pseudoreal, or essentially complex.

8.7.1

The Reality of Representations

Up to now, attention was paid to the spatial symmetries of a system. However, time-reversal symmetry as an additional symmetry can provide an extra degeneracy, sometimes referred to as the KRAMERS degeneracy. In this context, it is essential to verify if an irreducible representation is real or complex. The following three cases can be distinguished [35].

Definition 42 (potentially real, pseudoreal, essentially complex). *Consider a group $\mathcal{G}$ with a representation Γ . Dependent on the relationship between Γ and its conjugate complex representation Γ^* , Γ is either potentially real, pseudoreal, or essentially complex.*

1. **potentially real:** Γ is equivalent to a real representation and hence $\Gamma \sim \Gamma^*$.
2. **pseudoreal:** Γ is not equivalent to a real representation, but $\Gamma \sim \Gamma^*$.
3. **essentially complex:** $\Gamma \not\sim \Gamma^*$.

From the character system of a group, the relationship between Γ and Γ^* can be determined efficiently by applying the theorem of FROBENIUS and SCHUR⁴⁾.

Theorem 42 (Theorem of FROBENIUS and SCHUR). *Consider a finite group $\mathcal{G}$ of order g and a representation Γ of $\mathcal{G}$. For the characters $\chi(T^2)$ of the elements $T^2 = T \cdot T$, $T \in \mathcal{G}$, the following equation holds,*

$$\frac{1}{g} \sum_{T \in \mathcal{G}} \chi(T^2) = \begin{cases} 1 & \text{if } \Gamma \text{ is potentially real} \\ 0 & \text{if } \Gamma \text{ is essentially complex} \\ -1 & \text{if } \Gamma \text{ is pseudo-real} \end{cases} \quad (8.40)$$

Example 50 (The reality of the irreducible representations of $\overline{D}_3$). As an example the irreducible representations of the double group $\overline{D}_3$ are checked for being potentially real, pseudoreal, or essentially complex. To obtain the characters, the character table is calculated using **GTCharacterTable**. If the classes of the group and the characters of a representation are known, **GTReality** can be used for fur-

4) See [36] for a proof of the theorem.

Mathematica**GTReality**

At first the double group $\overline{D}_3$ is installed and the character table is calculated.

```
In[9]:= grp = GTInstallGroup[D3, GOREpresentation -> "SU(2)"]
{classes, characters, names} = GTCharacterTable[grp];
```

The standard representation has changed to SU(2)

```
Out[9]:= {Ee, Ee, C3z, C3z^-1, C2x, C2x, C2A, C2B, C2B, C2A, C3z^-1, C3z}
```

	Ee	2 C3z	2 C3z ⁻¹	3 C2x	3 C2x	Ee
Γ^1	1	1	1	1	1	1
Γ^2	1	1	-1	-i	i	-1
Γ^3	1	1	-1	i	-i	-1
Γ^4	1	1	1	-1	-1	1
Γ^5	2	-1	-1	0	0	2
Γ^6	2	-1	1	0	0	-2

$C_1 = \{Ee\}$

$C_2 = \{C_{3z}, C_{3z}^{-1}\}$

$C_3 = \{C_{3z}^{-1}, C_{3z}\}$

$C_4 = \{C_{2x}, C_{2B}, C_{2A}\}$

$C_5 = \{C_{2x}, C_{2A}, C_{2B}\}$

$C_6 = \{Ee\}$

GTReality is applied to each irreducible representation.

```
In[11]:= GTReality[classes, #] & /@ characters
```

```
Out[11]:= {potentially real, essentially complex,
           essentially complex, potentially real, potentially real, pseudo-real}
```

Figure 8.7 Application of **GTReality** to the irreducible representations of $\overline{D}_3$.

ther analysis. The application of **GTReality** to every irreducible representation of $\overline{D}_3$ is illustrated in Figure 8.7. As can be verified, there are three potentially real representations ($\Gamma^1, \Gamma^4, \Gamma^5$), one pseudoreal representation (Γ^6), and two essentially complex representations (Γ^2, Γ^3). As an alternative, it is possible to specify the option **GOREality** within the command **GTCharacterTable** to get the necessary information about the reality of the irreducible representations. An example is shown in Figure 8.8.

8.7.2

Spin-Independent Theory

The spin-independent HAMILTON operator $\hat{H}$ is a real and self-adjoint operator. Hence, all eigenvalues are real. Taking the complex conjugate of the

Mathematica**GOREality**

Information about the reality of irreducible representations can be obtained by specifying the option **GOREality** within **GTCharacterTable**.

```
In[12]:= grp = GTInstallGroup[D3, GOREpresentation -> "SU(2)"]
{classes, characters, names} = GTCharacterTable[grp, GOREality -> True];
```

The standard representation has changed to SU(2)

```
Out[12]:= {Ee, Ee-bar, C3z, C3z^-1, C2x, C2x-bar, C2A, C2B, C2B-bar, C2A-bar, C3z^-1, C3z}
```

	Ee	2 C _{3z}	2 C _{3z} ⁻¹	3 C _{2x}	3 C _{2x} -bar	Ee-bar	Reality
Γ^1	1	1	1	1	1	1	potentially real
Γ^2	1	1	-1	-i	i	-1	essentially complex
Γ^3	1	1	-1	i	-i	-1	essentially complex
Γ^4	1	1	1	-1	-1	1	potentially real
Γ^5	2	-1	-1	0	0	2	potentially real
Γ^6	2	-1	1	0	0	-2	pseudo-real

$C_1 = \{Ee\}$

$C_2 = \{\bar{C}_{3z}, C_{3z}^{-1}\}$

$C_3 = \{C_{3z}^{-1}, C_{3z}\}$

$C_4 = \{C_{2x}, C_{2B}, \bar{C}_{2A}\}$

$C_5 = \{\bar{C}_{2x}, C_{2A}, \bar{C}_{2B}\}$

$C_6 = \{\bar{Ee}\}$

Figure 8.8 Specifying the option **GOREality** within the command **GTCharacterTable** prints the information about the reality of the irreducible representations.

SCHRÖDINGER equation, one obtains

$$\hat{H}(\mathbf{r}, t)\phi(\mathbf{r}, t)^* = i\hbar \frac{\partial}{\partial(-t)} \phi(\mathbf{r}, t)^* . \quad (8.41)$$

As can be seen, complex conjugation changes the sign of the time. Hence, it can be understood as the time-reversal operator for the case of the spin-independent SCHRÖDINGER equation.

For time-independent potentials, the eigenfunctions $\phi_1^p(\mathbf{r}), \dots, \phi_{d_p}^p(\mathbf{r})$ of a d_p -times degenerated energy level E_p transform like an irreducible representation Γ^p of the group of the SCHRÖDINGER equation $\mathcal{G}_{\text{SEQ}}$. Also, the complex conjugate functions $\phi_1^p(\mathbf{r})^*, \dots, \phi_{d_p}^p(\mathbf{r})^*$ are eigenfunctions of the SCHRÖDINGER equation. Thus, it remains to verify if they are linearly independent of $\phi_1^p(\mathbf{r}), \dots, \phi_{d_p}^p(\mathbf{r})$. If so, they extend the subspace and hence E_p is a $2d_p$ -times degenerate eigenvalue, with the basis functions $\phi_1^p(\mathbf{r}), \dots, \phi_{d_p}^p(\mathbf{r}), \phi_1^p(\mathbf{r})^*, \dots, \phi_{d_p}^p(\mathbf{r})^*$.

Theorem 43 (Time-reversal symmetry for the spin-independent SCHRÖDINGER equation). *Let Γ^p be a d_p -dimensional unitary irreducible representation of a group $\mathcal{G}$ with eigenfunctions $\phi_1^p(\mathbf{r}), \dots, \phi_{d_p}^p(\mathbf{r})$. If Γ^p is pseudoreal or essentially complex, the conjugate complex functions $\phi_1^p(\mathbf{r})^*, \dots, \phi_{d_p}^p(\mathbf{r})^*$ are linearly independent of $\phi_1^p(\mathbf{r}), \dots, \phi_{d_p}^p(\mathbf{r})$.*

A proof of the theorem can be found in [36].

8.7.3

Spin-Dependent Theory

In the case of the PAULI equation where a spin-orbit coupling term is present the HAMILTON operator $\hat{H}$ becomes complex valued. The conjugate complex of $\hat{H}$ can be expressed in terms of the PAULI matrix $\underline{\sigma}_y$,

$$\hat{H}^* = \underline{\sigma}_y^{-1} \cdot \hat{H} \cdot \underline{\sigma}_y = \underline{\sigma}_y \cdot \hat{H} \cdot \underline{\sigma}_y. \quad (8.42)$$

For a time-independent potential, the following eigenvalue equation follows from the PAULI equation,

$$\hat{H} \cdot \Phi_m^p = E_p \Phi_m^p. \quad (8.43)$$

The spinor function Φ_m^p is the m th basis function of the irreducible representation Γ^p of the group of the PAULI equation $\mathcal{G}_{\text{PEQ}}$. Taking the conjugate complex of equation (8.43) and using (8.42), it is possible to obtain the following equation,

$$\hat{H} \cdot (\underline{\sigma}_y \Phi_m^{p*}) = E_p (\underline{\sigma}_y \Phi_m^{p*}). \quad (8.44)$$

Therefore, $(\underline{\sigma}_y \Phi_m^{p*})$ is another eigenfunction of the spin-dependent HAMILTON operator. The time-reversal operator is given by a combination of $\underline{\sigma}_y$ and applying complex conjugation. Analogously to the spin-independent case, it has to be investigated if $(\underline{\sigma}_y \Phi_m^{p*})$ is linear independent of the functions $\Phi_n^p, n = 1, \dots, d_p$. If $(\underline{\sigma}_y \Phi_m^{p*})$ is linear independent of $\Phi_n^p, n = 1, \dots, d_p$, then E_p is a $2d_p$ -times degenerate eigenvalue of $\hat{H}$. The question of linear dependence is answered by the following theorem.

Theorem 44 (Time-reversal symmetry for the spin-dependent PAULI equation). *Let Γ^p be a d_p -dimensional unitary irreducible representation of a group $\mathcal{G}$ with eigenfunctions $\Phi_1^p(\mathbf{r}), \dots, \Phi_{d_p}^p(\mathbf{r})$. If Γ^p is potentially real or essentially complex, the spinors $(\underline{\sigma}_y \Phi_1^{p*}), \dots, (\underline{\sigma}_y \Phi_{d_p}^{p*})$ are linearly independent of $\Phi_1^p(\mathbf{r}), \dots, \Phi_{d_p}^p(\mathbf{r})$.*

As in the previous section, Theorem 44 is given without proof. By comparing Theorems 43 and 44, it turns out that the conditions for additional degeneracy due to time-reversal symmetry differ tremendously on taking into account the spin or not. Whereas additional degeneracy can be expected if the irreducible representation is pseudoreal or essentially complex for spin-independent systems, an additional degeneracy occurs if the irreducible representation is potentially real or essentially complex in the case of spin-dependent systems.

9

Electronic Structure Calculations

The Theory of Groups is usually associated with the strictest logical treatment Various mathematical tools have been tried for digging down to the basis of physics, and at present this tool seems more powerful than any other.

Sir A. Eddington
(*New Pathways in Science, Messenger Lectures 1934*)

This chapter introduces the application of group theory to electronic structure calculations. On one hand, group theory can be applied to simplify the construction of effective model Hamiltonians. On the other hand, the symmetry of the underlying system leads to strong constraints, e.g., with respect to the degeneracy of energy levels and band structures. Throughout the chapter, these concepts are explained on the basis of tight-binding and plane-wave Hamiltonians. Both approaches are supported within GTPack. The chapter closes with specific examples, such as carbon nanotubes, semiconductors with strong spin-orbit coupling and perovskites.

9.1

Solution of the Schrödinger Equation for a Crystal

In the following, the solution of the SCHRÖDINGER equation¹⁾

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \phi(\mathbf{r}) = E\phi(\mathbf{r}) \quad (9.1)$$

for a lattice periodic potential is discussed. As introduced in Section 4.2, the symmetry of a lattice periodic crystal is described by the space group $\mathcal{R}$. The crystal

1) A one-particle picture is assumed due to the discussion of model Hamiltonians. A formulation of the problem in terms of density functional theory is not necessary.

potential $V(\mathbf{r})$ is invariant under all operations of the group, i.e.,

$$\hat{P}(T)V(\mathbf{r}) = V(\mathbf{r}), \quad \forall T \in \mathcal{R}. \quad (9.2)$$

Consequently, for elements $T = \{\underline{1}|\mathbf{t}_T\}$ of the translation group $\mathcal{T}$ it holds,

$$\hat{P}(T)V(\mathbf{r}) = V(\mathbf{r} - \mathbf{t}_T) = V(\mathbf{r}), \quad \forall T \in \mathcal{T}. \quad (9.3)$$

According to Section 6.1 the solution of (9.1) has to be a BLOCH function, i.e., an eigenfunction of the irreducible representations $\Gamma^{\mathbf{k}}$ of $\mathcal{T}$,

$$\phi_{\mathbf{k}}(\mathbf{r} + \mathbf{t}) = e^{i\mathbf{k}\cdot\mathbf{t}}\phi_{\mathbf{k}}(\mathbf{r}), \quad \phi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r}), \quad u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{t}). \quad (9.4)$$

That means, in the case of an infinite solid, the total wave function $\phi(\mathbf{r})$ in (9.1) explicitly depends on a $\mathbf{k}$ -point of the BRILLOUIN zone, $\phi_{\mathbf{k}}(\mathbf{r})$. In basis set methods, the unknown wave function $\phi_{\mathbf{k}}(\mathbf{r})$ is expanded in terms of a linear combination of N_b BLOCH functions $\psi_n(\mathbf{k}, \mathbf{r})$ constructed from known basis functions,

$$\phi_{\mathbf{k}}(\mathbf{r}) = \sum_{n=1}^{N_b} c_n(\mathbf{k}) \psi_n(\mathbf{k}, \mathbf{r}). \quad (9.5)$$

Such BLOCH functions could be constructed from plane waves or from localized orbitals as will be discussed in more detail later. By using equation (9.5) together with (9.1) a set of N_b equations to calculate the coefficients $c_n(\mathbf{k})$ ($n = 1, \dots, N_b$) follows,

$$\sum_{n=1}^{N_b} c_n(\mathbf{k}) \left\{ \left(\psi_m(\mathbf{k}, \mathbf{r}), \hat{H} \psi_n(\mathbf{k}, \mathbf{r}) \right) - E(\mathbf{k}) \left(\psi_m(\mathbf{k}, \mathbf{r}), \psi_n(\mathbf{k}, \mathbf{r}) \right) \right\} = 0. \quad (9.6)$$

Hence, the SCHRÖDINGER equation (9.1) is transformed into a matrix eigenvalue problem given by²⁾

$$\underline{\underline{H}}(\mathbf{k}) \mathbf{c}(\mathbf{k}) = E(\mathbf{k}) \underline{\underline{S}}(\mathbf{k}) \mathbf{c}(\mathbf{k}). \quad (9.7)$$

The dimension of the Hamiltonian matrix $\underline{\underline{H}}$ and of the overlap matrix $\underline{\underline{S}}$ is given by the dimension of the basis set N_b .

9.2

Symmetry Properties of Energy Bands

Symmetry and Compatibility	
GTCompatibility	Generates a list of compatibility relations

2) $\mathbf{c}(\mathbf{k}) = (c_1(\mathbf{k}), c_2(\mathbf{k}), \dots, c_{N_b}(\mathbf{k}))^T$ is the vector containing the expansion coefficients.

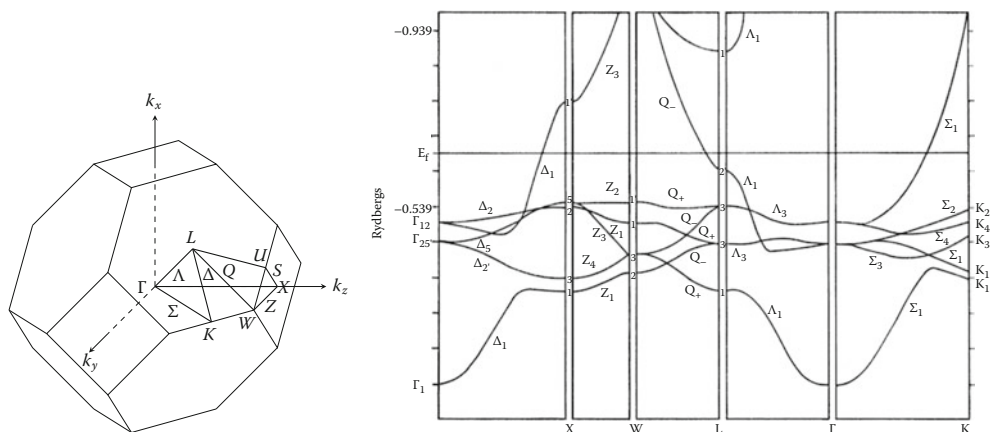


Figure 9.1 BRILLOUIN zone of the fcc structure and band structure of Cu along lines of high symmetry in the BRILLOUIN zone. The band structure is taken from [121] (BSW notation used). (With permission, Copyright © 1963 American Physical Society.)

In the following, general symmetry properties of band structures are discussed for the example of copper (Cu). Cu crystallizes in an fcc lattice with a one-atomic basis having the symmorphic space group $Fm\bar{3}m$ (#225). In general, if not mentioned otherwise the discussion is restricted to symmorphic space groups hereafter. The band structure of Cu, according to BURDICK [121] is shown in Figure 9.1³⁾. As typical for transition metals, it is characterized by narrow d -bands formed from the atomic d -levels, hybridizing with broad sp -bands.

The degeneracy of the electronic energy bands depends on the $\mathbf{k}$ -point in the BRILLOUIN zone. For example, the 3-fold degenerate energy level $\Gamma_{25'}$ at the Γ point is split into a one-fold and a two-fold degenerate band along the path Δ , connecting Γ and X . At the X point the band with symmetry Δ_5 is split at the energy level denoted by X_5 into two bands along the path connecting X and W .

The degeneracy of bands as well as allowed or forbidden crossings of bands follow from the fundamental theorem of irreducible representations of symmorphic space groups (see Section 6.4). It will be one goal of the subsequent discussion to demonstrate that the classification of eigenvalues as in the example of Cu can be done automatically.

To proceed, some remarks on the notation of the irreducible representations are necessary. As discussed in Section 5.3.3, different schemes are used in the literature. In solid-state physics the nomenclature corresponding to BOUCKAERT, SMOLUCHOWSKI, and WIGNER (BSW) is popular [89], which is also used in Figure 9.1. A molecular notation, commonly used in quantum chemistry is based on the work of MULLIKEN [90, 91]. Another scheme goes back to BETHE [88].

- 3) The band structure is plotted along certain high symmetry paths within the BRILLOUIN zone. Such paths can be generated automatically by using **GTBZPath** within GTPack (see Example 38).

Table 9.1 Notation of the irreducible representations at Γ and X of the BRILLOUIN zone of the fcc structure corresponding to BETHE, BOUCKAERT, SMOLUCHOWSKI and WIGNER (BSW), and MULLIKEN. The point groups at Γ and X are O_h and D_{4h} , respectively.

Notations	k	Irreducible representations									
Bethe	Γ	Γ^1	Γ^2	Γ^3	Γ^4	Γ^5	Γ^6	Γ^7	Γ^8	Γ^9	Γ^{10}
BSW		Γ_1	Γ_2	Γ_{12}	$\Gamma_{15'}$	$\Gamma_{25'}$	$\Gamma_{1'}$	$\Gamma_{2'}$	$\Gamma_{12'}$	Γ_{15}	Γ_{25}
Mulliken		A_{1g}	A_{2g}	E_g	T_{1g}	T_{2g}	A_{1u}	A_{2u}	E_u	T_{1u}	T_{2u}
Bethe	X	Γ^1	Γ^2	Γ^3	Γ^4	Γ^5	Γ^6	Γ^7	Γ^8	Γ^9	Γ^{10}
BSW		X_1	X_2	X_3	X_4	X_5	$X_{1'}$	$X_{2'}$	$X_{3'}$	$X_{4'}$	$X_{5'}$
Mulliken		A_{1g}	B_{1g}	B_{2g}	A_{2g}	E_g	A_{1u}	B_{1u}	B_{2u}	A_{2u}	E_u

Table 9.1 gives the correspondence of the three notations for the points Γ and X of the fcc structure.

The construction of the character table by means of `GTCharacterTable` allows one to select one of the three schemes.

9.2.1
Degeneracy and Symmetry of Energy Bands

The degeneracy of the energy eigenvalues $E_n(\mathbf{k})$ of a band structure can be concluded from the fundamental theorem for irreducible representations of symmorphic space groups. The system is characterized by a space group $\mathcal{R}$ with a corresponding crystallographic point group $\mathcal{G}_0$. At a certain wave vector $\mathbf{k}$ the group of the wave vector is $\mathcal{R}(\mathbf{k})$ having the point group $\mathcal{G}_0(\mathbf{k})$. The orders of the groups are $\text{ord}\mathcal{G}_0 = g_0$ and $\text{ord}\mathcal{G}_0(\mathbf{k}) = g_0(\mathbf{k})$. The numbers of vectors in the star is given by $M(\mathbf{k}) = g_0/g_0(\mathbf{k})$, as discussed in Section 6.3. Points of different symmetry in the BRILLOUIN zone will be considered.

1. *general $\mathbf{k}$ -point*

A general point of the BRILLOUIN zone will be transformed into itself or an equivalent point only by the point group operation $\{\underline{1}|0\}$, i.e., the group of the wave vector $\mathcal{G}_0(\mathbf{k})$ is given by the trivial group having only one 1-dimensional irreducible representation ($d = 1$). The star of $\mathbf{k}$ consists of $M(\mathbf{k}) = g_0/g_0(\mathbf{k}) = g_0$ vectors. The dimension of the irreducible representation of the space group $\mathcal{R}$ is therefore $d \cdot M(\mathbf{k}) = g_0$. The g_0 BLOCH functions with $\mathbf{k}$ -vectors $\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_{g_0}$ of the star are basis functions of the irreducible representation of $\mathcal{R}$. The corresponding eigenvalues are degenerate

$$E_n(\underline{\mathbf{R}}_i\mathbf{k}) = E_n(\mathbf{k}_i) = E_n(\mathbf{k}), \quad i = 1, \dots, g_0, \quad \underline{\mathbf{R}}_i \in \mathcal{G}_0. \tag{9.8}$$

Thus, if the band structure in a $1/g_0$ part of the BRILLOUIN zone is known, it is known in the whole BZ.

In the case of the fcc structure having the point group $\mathcal{G}_0 = O_h$, ($\text{ord}\mathcal{G}_0 = 48$), a $1/48$ part of the BRILLOUIN zone is enough to calculate the band structure throughout the BRILLOUIN zone. This so-called irreducible wedge of the BRILLOUIN zone is shown in Figure 9.1.

2. Γ point

In the case of the Γ point $\mathcal{G}_0(\mathbf{k}) \equiv \mathcal{G}_0$ holds. The star consists only of the vector $\mathbf{k} = 0$. The basis functions of the space group $\mathcal{R}$ are therefore BLOCH functions with symmetries according to the crystallographic point group. Referring to Figure 9.1, and the character table of O_h , the irreducible representations $\Gamma_{25'}$ (T_{2g}) and Γ_{12} (E_g) correspond to threefold and twofold degenerate states, respectively. The representation Γ_1 (A_{1g}) is the identity representation and corresponds to functions invariant under all operations of the point group. Such a representation corresponds to BLOCH functions constructed from s -orbitals if localized orbitals are used during the calculation.

3. $\mathcal{G}_0(\mathbf{k}) \subset \mathcal{G}_0$

Symmetry points (except of Γ) and points on symmetry lines or planes having proper and nontrivial subgroups $\mathcal{G}_0(\mathbf{k}) \subset \mathcal{G}_0$ belong to this category. Because of $g_0(\mathbf{k}) < g_0$ the number of vectors in the star is $M(\mathbf{k}) > 1$. Let $E_n(\mathbf{k})$ be a d -fold degenerate energy eigenvalue with respect to $\mathcal{G}_0(\mathbf{k})$. This leads to a $d \cdot M(\mathbf{k})$ -fold degeneracy with respect to $\mathcal{R}$. At each vector of the star the same energy eigenvalue appears

$$E_n(\mathbf{k}_i) = E_n(\mathbf{k}), \quad i = 1, \dots, M(\mathbf{k}). \quad (9.9)$$

Additionally, this energy is d -fold degenerate.

This discussion can be easily extended to non-symmorphic space groups.

9.2.2

Compatibility Relations and Crossing of Bands

Within the Cu band structure shown in Figure 9.1, the groups $\mathcal{G}_0(\mathbf{k})$ are given by O_h at Γ , D_{4h} at X , and C_{4v} along the path Δ connecting Γ and X . The group C_{4v} is a subgroup of the full cubic group O_h . Irreducible representations at Γ are therefore reducible along the line Δ , and can be decomposed into a CLEBSCH–GORDAN sum with respect to the irreducible representations of C_{4v} . The number n_p^q how often an irreducible representation Γ'^p of the group $\mathcal{G}' \subset \mathcal{G}$ occurs within a representation Γ^q , denoting an irreducible representation of $\mathcal{G}$, is given by (Theorem 21 in Section 5.3.4)

$$n_p^q = \frac{1}{g} \sum_{T \in \mathcal{G}} [\chi'^p(T)]^* \chi^q(T). \quad (9.10)$$

A representation Γ'^p is called *compatible* with a representation Γ^q if $n_p^q > 0$. Compatibility relations can be verified using GTPack as will be shown within the following example.

Example 51 (Compatibility relations between C_{4v} and O_h) The application of the GTPack command **GTCompatibility** calculating compatibility relations is shown for the example of $C_{4v} \subset O_h$. From the characters given in Table 9.2 and equation (9.10) it follows

$$T_{2g} \simeq B_2 \oplus E, \tag{9.11}$$

and

$$E_g \simeq A_1 \oplus B_1. \tag{9.12}$$

Alternatively, according to Figure 9.2, applying **GTCompatibility** leads to a similar result. The point group symbols are the input of **GTCompatibility**.

The inspection of the band structure in Figure 9.1 demonstrates that bands belonging to the same irreducible representation do not cross. The degeneracy of a band is given by the dimension of the related irreducible representation. A crossing of bands to the same irreducible representation would cause a degeneracy

Table 9.2 Information from the character tables of C_{4v} and O_h to evaluate (9.10). Characteristic elements of the classes are: $C_1 - E, C_2 - IC_{2x}, C_3 - IC_{2a}, C_4 - C_{4z}^{-1}, C_5 - C_{2z}$.

Classes		C_1	C_2	C_3	C_4	C_5
Elements/Class		1	2	2	2	1
C_{4v}	A_1	1	1	1	1	1
	A_2	1	-1	-1	1	1
	B_1	1	1	-1	-1	1
	B_2	1	-1	1	-1	1
	E	2	0	0	0	-2
O_h	A_{1g}	1	1	1	1	1
	T_{2g}	3	-1	1	-1	-1
	E_g	2	2	0	0	2

Mathematica
GTCompatibility

Calculation of the compatibility relations using GTCompatibility for the point groups O_h and C_{4v} .

In[8]:= **GTCompatibility**[**Oh**, **C4v**, **GOirepNotation** -> "Mulliken"]

A_{1g}	A_{2u}	A_{1u}	A_{2g}	E_u	E_g	T_{1g}	T_{2g}	T_{1u}	T_{2u}
{A1}	{B2}	{A2}	{B1}	{A2, B2}	{A1, B1}	{A2, E}	{B2, E}	{A1, E}	{B1, E}

Figure 9.2 Compatibility of irreducible representations occurring at the symmetry point Γ and the symmetry line Δ in the BRILLOUIN zone of the fcc structure.

higher than allowed. Tight-binding Hamiltonians, as discussed in more detail later in this chapter, can be used to discuss the hybridization effects in greater detail. A targeted switch-off of tight-binding parameters allows one to study bands belonging to different angular momenta or groups of atoms separately.

Task 29 (Compatibility relations). Investigate the compatibility relations between the points Γ and L along the line Λ for the fcc structure. The groups $\mathcal{G}_0(\mathbf{k})$ are C_{3v} along Λ and D_{3d} at L. First, use **GTCompatibility**, and, second, verify the result applying equation (9.10) implemented in **GTirep**. Compare the results with Figure 9.1.

9.3

Symmetry-Adapted Functions

Symmetry-adapted functions	
GTPwSymmetrizePW	Generates symmetrized plane waves
GTmolGetMolecule	Retrieves molecular data from a data base
GTmolPermutationRep	Generates the permutation representation

The use of plane waves or localized functions as basis functions within the expansion of the wave function within the SCHRÖDINGER equation (9.1) leads to an eigenvalue problem as given in equation (9.7). The eigenvalue problem can be simplified by applying a basis transformation in such a way that the eigenvalue problem is block diagonalized. This form can be achieved by expanding in terms of the basis functions of the irreducible representation of the symmetry group of the Hamiltonian, as follows from the WIGNER–ECKART Theorem (cf. Section 5.6). The computational demand is decreased, since it remains to solve eigenvalue equations for the sub-blocks, which are lower in dimension. Subsequently, it will be demonstrated for the example of plane waves and localized orbitals, how symmetry-adapted basis functions can be constructed.

9.3.1

Symmetry-Adapted Plane Waves

A plane wave $\psi_{\mathbf{G}}(\mathbf{k}, \mathbf{r})$ can be characterized by a reciprocal lattice vector $\mathbf{G}$ as⁴⁾

$$\psi_{\mathbf{G}}(\mathbf{k}, \mathbf{r}) = e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}. \quad (9.13)$$

$\psi_{\mathbf{G}}$ is a BLOCH function, since

$$\psi_{\mathbf{G}}(\mathbf{k}, \mathbf{r} + \mathbf{t}) = e^{i(\mathbf{k}+\mathbf{G})\cdot(\mathbf{r}+\mathbf{t})} = e^{i\mathbf{k}\cdot\mathbf{t}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}. \quad (9.14)$$

4) A normalization factor is neglected. $\mathbf{G}$ will be used for the reciprocal lattice vector instead of $\mathbf{K}$ for a clear distinction from vectors $\mathbf{k}$ in the BRILLOUIN zone.

A general wave function of a solid can be expressed as a sum over plane waves,

$$\phi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}}(\mathbf{k}) \psi_{\mathbf{G}}(\mathbf{k}, \mathbf{r}) . \quad (9.15)$$

For a point group $\mathcal{G}_0$ and a given wave vector $\mathbf{k}$, the associated point group of the wave vector is denoted by $\mathcal{G}_0(\mathbf{k})$. A symmetrized plane wave, which transforms as the n th row of an irreducible representation Γ^p of $\mathcal{G}_0(\mathbf{k})$ can be constructed by applying the projection operator $\hat{P}_{m,n}^p$ (see equation (5.61)),

$$\hat{P}_{n,n}^p e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} = \frac{l_p}{g_0(\mathbf{k})} \sum_{T \in \mathcal{G}_0(\mathbf{k})} \Gamma_{n,n}^p(T)^* \hat{P}(T) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} . \quad (9.16)$$

Since $T = \{\underline{\mathbb{R}}|0\} \in \mathcal{G}_0(\mathbf{k})$ and

$$\hat{P}(T) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} = e^{i(\mathbf{k}+\mathbf{G})\cdot\underline{\mathbb{R}}^{-1}\mathbf{r}} = e^{i\underline{\mathbb{R}}(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} = e^{i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}} \quad (9.17)$$

an initial plane wave will be transformed into a linear combination of plane waves having the required symmetry properties.

Example 52 (Construction of symmetrized plane waves in GTPack). Symmetrized plane waves can be constructed in GTPack by applying the command **GTPwSymmetrizePW** , as shown in Figure 9.3. The example discusses the H point in the BRILLOUIN zone of a bcc lattice (see Example 38), where the corresponding point group $\mathcal{G}_0$ is O_h . It follows that H has the same symmetry, i.e., $\mathcal{G}_0(H) = \mathcal{G}_0 = O_h$. $\mathbf{H}_{12}$ (E_g) is a two-dimensional and $\mathbf{H}_{15}$ (T_{1u}) a three-dimensional irreducible representation, respectively. A single plane wave with $\mathbf{k}_0 = (0, 1, 0)(2\pi)/a$ is used to construct the basis function to H_{12} and H_{15} . The first table in Figure 9.3 shows the equivalent wave vectors $\mathbf{k} + \mathbf{G}$ that appear eventually in the symmetrized basis functions of the corresponding irreducible representation, where the input plane wave is denoted by ψ_5 . The basis functions are presented in two forms, first, as a linear combination of the ψ_i and, second, evaluated and expressed in terms of sine and cosine functions. As can be seen, ψ_5 occurs in both basis functions belonging to $\mathbf{H}_{12}$ and the first basis function belonging to $\mathbf{H}_{15}$. That means, in the case of $\mathbf{H}_{15}$, not all the basis functions could be constructed by applying the projection operator $\hat{P}_{nn}^{15}$ to an initial plane wave with the wave vector $\mathbf{k}_0 = (0, 1, 0)(2\pi)/a$. To obtain the other two functions, the operator $\hat{P}_{m,n}^p$ has to be applied, which projects a basis function $\varphi_n^p(\mathbf{r})$ transforming as the n th row of Γ^p into a basis function $\varphi_m^p(\mathbf{r})$ belonging to the m th row. Within **GTPwSymmetrizePW** , the option **GOProjection** controls the index pairs $\{n, m\}$. In summary, the steps of the calculation of the basis functions of $\mathbf{H}_{15}$ are

$$\hat{P}_{1,1}^{15} e^{i\mathbf{k}_0\cdot\mathbf{r}} = \varphi_1^{15}(\mathbf{r}) , \quad \hat{P}_{3,1}^{15} \varphi_1^{15}(\mathbf{r}) = \varphi_3^{15}(\mathbf{r}) , \quad \hat{P}_{2,1}^{15} \varphi_1^{15}(\mathbf{r}) = \varphi_2^{15}(\mathbf{r}) . \quad (9.18)$$

Task 30 (Symmetry-adapted plane waves). Construct symmetrized plane waves at the point X of the BRILLOUIN zone of the face-centered cubic structure. Investigate the irreducible representations X_1 , X_4 , and X_5 .

Mathematica**GTPwSymmetrizePW**

Install the point group O_h and calculate the character table.

```
In[8]:= oh = GTInstallGroup[Oh, GVerbose -> False];
ohct = GTCharacterTable[oh, GOIrepNotation -> "Bouckaert", GVerbose -> False];
```

The irreducible representation H_{12} is the sixth irreducible representation in the calculated character table. The initial $\mathbf{k}$ -vector is $(0,1,0)$.

```
In[10]:= GTPwSymmetrizePW[ohct, {0, 1, 0}, 6, GOMethod -> "Cornwell"];
```

	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	ψ_6
K_x	-1	0	0	0	0	1
K_y	0	-1	0	0	1	0
K_z	0	0	-1	1	0	0

Irep	n	Symmetrized linear combinations
12	1	$\frac{-\psi_1}{2\sqrt{3}} + \frac{-\psi_2}{2\sqrt{3}} - \frac{\psi_3}{\sqrt{3}} - \frac{\psi_4}{\sqrt{3}} + \frac{\psi_5}{2\sqrt{3}} + \frac{-\psi_6}{2\sqrt{3}}$ $\frac{\cos[2\pi x] + \cos[2\pi y] - 2\cos[2\pi z]}{\sqrt{3}}$
	2	$-\frac{\psi_1}{2} + \frac{\psi_2}{2} + \frac{\psi_3}{2} - \frac{\psi_6}{2}$ $-\cos[2\pi x] + \cos[2\pi y]$

H_{15} is the ninth irreducible representation in the calculated character table.

```
In[11]:= GTPwSymmetrizePW[ohct, {0, 1, 0}, 9, GOMethod -> "Cornwell",
GVerbose -> False, GOProjection -> {{1, 1}, {1, 3}, {1, 2}}];
```

Irep	n	Symmetrized linear combinations
15	1	$-\frac{\psi_2}{\sqrt{2}} + \frac{\psi_3}{\sqrt{2}}$ $i\sqrt{2}\sin[2\pi y]$
	2	$-\frac{\psi_3}{\sqrt{2}} + \frac{\psi_4}{\sqrt{2}}$ $i\sqrt{2}\sin[2\pi z]$
	3	$-\frac{\psi_1}{\sqrt{2}} + \frac{\psi_6}{\sqrt{2}}$ $i\sqrt{2}\sin[2\pi x]$

Figure 9.3 Construction of symmetrized plane waves at H in the body-centered structure. O_h is $G_0(\mathbf{k})$ in this case.

9.3.2

Localized Orbitals

A BLOCH function can be constructed starting from localized atomic wave functions $\varphi_n(\mathbf{r})$ via

$$\psi_n(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{t}} e^{i\mathbf{k}\cdot\mathbf{t}} \varphi_n(\mathbf{r} - \mathbf{t}). \quad (9.19)$$

The index n is an abbreviation for the quantum numbers characterizing the function $\varphi_n(\mathbf{r})$. The summation runs over all lattice vectors $\mathbf{t}$.

Considering the symmetry operations $T_R = \{\underline{R} | 0\}$ and $T_T = \{\underline{1} | \mathbf{t}\}$, expressing a pure rotation $\underline{R}$ and a translation by the lattice vector $\mathbf{t}$, respectively, it is possible to discuss the transformation behavior of (9.19). Applying the rotation T_R to the

BLOCH function (9.19) gives

$$\hat{P}(T_R)\psi_n(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{t}} e^{i\mathbf{k}\cdot\mathbf{t}} \hat{P}(T_R) \hat{P}(T_T) \varphi_n(\mathbf{r}) , \quad (9.20)$$

$$= \frac{1}{\sqrt{N}} \sum_{\mathbf{t}} e^{i\mathbf{k}\cdot\mathbf{t}} \varphi_n(\underline{\mathbb{R}}^{-1}\mathbf{r} - \mathbf{t}) . \quad (9.21)$$

The second line follows from the commutation of rotation and translation for rotations belonging to the point group of the lattice. Introducing $\mathbf{t} = \underline{\mathbb{R}}^{-1}\tilde{\mathbf{t}}$ in (9.21) leads to

$$\hat{P}(T_R)\psi_n(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\tilde{\mathbf{t}}} e^{i\mathbf{k}\cdot\underline{\mathbb{R}}^{-1}\tilde{\mathbf{t}}} \varphi_n(\underline{\mathbb{R}}^{-1}(\mathbf{r} - \tilde{\mathbf{t}})) . \quad (9.22)$$

The properties of the scalar product together with the orthogonality of $\underline{\mathbb{R}}$ finally result in

$$\begin{aligned} \hat{P}(T_R)\psi_n(\mathbf{k}, \mathbf{r}) &= \frac{1}{\sqrt{N}} \sum_{\tilde{\mathbf{t}}} e^{i\mathbf{k}\cdot\underline{\mathbb{R}}^{-1}\tilde{\mathbf{t}}} \varphi_n(\underline{\mathbb{R}}^{-1}(\mathbf{r} - \tilde{\mathbf{t}})) , \\ &= \frac{1}{\sqrt{N}} \sum_{\tilde{\mathbf{t}}} e^{i\mathbf{k}\cdot\tilde{\mathbf{t}}} \hat{P}(T_{\tilde{T}}) \hat{P}(T_R) \varphi_n(\mathbf{r}) , \end{aligned} \quad (9.23)$$

where $\tilde{T} = \{\underline{\mathbb{1}} \mid \tilde{\mathbf{t}}\}$ was used. The summation in (9.23) runs over all lattice sites, i.e., $\tilde{\mathbf{t}}$ can be renamed in $\mathbf{t}$. Per definition of $\mathcal{G}_0(\mathbf{k})$, it follows $T_R \in \mathcal{G}_0(\mathbf{k}) \Leftrightarrow \underline{\mathbb{R}}\mathbf{k} \equiv \mathbf{k}$. Thus,

$$\hat{P}(T_R)\psi_n(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{t}} e^{i\mathbf{k}\cdot\mathbf{t}} \hat{P}(T_T) \hat{P}(T_R) \varphi_n(\mathbf{r}) . \quad (9.24)$$

Consequently, with respect to point group symmetry the BLOCH function transforms similarly to the atomic wave function $\varphi_n(\mathbf{r})$. Hence, if $\varphi_n(\mathbf{r})$ transforms corresponding to a certain irreducible representation of the group $\mathcal{G}_0(\mathbf{k})$, the BLOCH function does too. In spherical potentials like the COULOMB potential, the functions $\varphi_n(\mathbf{r})$ can be separated into a radial part and an angular part given by spherical harmonics. The projection operator can therefore be used to construct linear combinations of spherical harmonics transforming as a certain irreducible representation of the group under consideration (**GTWignerProjectionOperator**).

In the case of molecules, the translational symmetry is absent. Here, the ansatz to solve SCHRÖDINGER's equation does not contain a linear combination of BLOCH functions, but a linear combination of atomic orbitals located at the positions of the atoms. Those linear combinations can be built in such a form that symmetry-adapted linear combinations (SALC's) are formed, transforming as a certain row of an irreducible representation of the symmetry group of the molecule, as will be explained in the following example.

Example 53 (Symmetry-adapted linear combinations for the benzene molecule). A schematic picture of the benzene molecule C_6H_6 is shown in Figure 9.4. The discussion will concentrate on the π -electron system (six $2p_z$ -orbitals, perpendicular to the σ -bonds in the x - y -plane).⁵⁾ The symmetry group G_0 of benzene is given by D_{6h} . Starting from the p_z -orbitals, six SALC's are constructed. The symmetry operations of D_{6h} interchange the orbitals in the benzene ring and additionally might also change the orientation of the p_z -orbitals, i.e., change the sign. The interchange or permutation of the orbitals can be used to construct a six-dimensional faithful representation Γ of D_{6h} , as shown in Figure 9.5. For one element of each class, the position in the element list of G_0 is found. For D_{6h} , the rotation matrices $\underline{R}$ are block-diagonal, where the element $R_{3,3}$ indicates a sign change of the z -coordinate and with that the sign change of the p_z -orbitals. The permutation representation itself is constructed by applying **GTMolPermutation-Rep**.⁶⁾ Taking the character system of the permutation representation together with the estimated sign changes gives the character system of the faithful representation for the benzene molecule having D_{6h} symmetry. The decomposition of the faithful representation Γ into irreducible representations of D_{6h} gives

$$\Gamma = A_{2u} \oplus B_{2g} \oplus E_{1g} \oplus E_{2u} . \quad (9.25)$$

The decomposition also describes the symmetry of the six SALC's, where two of them belong to the one-dimensional representations A_{2u} and B_{2g} and four to the two 2-dimensional representations E_{1g} and E_{2u} (see Figure 9.6 for a character table).

Here, the character projection operator

$$\hat{P}^p = \frac{l_p}{g} \sum_{T \in G} [\chi^p(T)]^* \hat{P}(T) \quad (9.26)$$

is applied to construct the SALC's for the two one-dimensional irreducible representations.

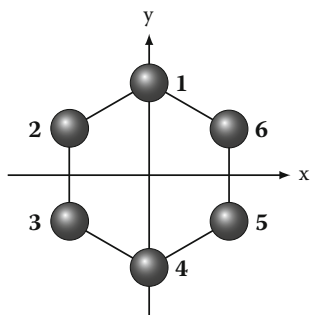


Figure 9.4 Molecular graph of benzene. Carbon atoms numbered for discussion of symmetry operations.

5) For a more detailed discussion see [37].

6) Molecular databases and the permutation representation are discussed in more detail in Chapter 13.

Mathematica

GTMolGetMolecule, GTMolPermutationRep

Installation of the point group D_{6h} and calculation of the character table.

```
In[8]:= d6h = GTInstallGroup[D6h]; ctab = {classes, chars, names} =
      GTCharacterTable[d6h, GOIrepNotation -> "Mulliken", GOVerbose -> False];
      The standard representation has changed to O(3)
```

Find the position of a class representative of each class within the group.

```
In[9]:= reps = First[#] & /@GTClasses[d6h]; pos = Position[d6h, #] & /@reps // Flatten
Out[9]:= {1, 21, 9, 23, 11, 3, 14, 4, 15, 13, 2, 20}
```

Find sign changes of p_z -orbitals for the considered elements.

```
In[10]:= signc = GTGetMatrix[#][[3, 3]] & /@reps
Out[10]:= {1, -1, 1, -1, 1, -1, 1, -1, 1, -1, 1, -1}
```

Read data for benzene and construct the permutation representation.

```
In[11]:= benzene = GTMolGetMolecule["Molecules", 4]; prep = GTMolPermutationRep[benzene];
```

Calculate the characters of the faithful representation from the permutation representation and the information about the sign changes of the orbitals.

```
In[12]:= charp = Tr[#] & /@Flatten[Take[prep, {#}] & /@pos, 1];
      charf = charp * signc
Out[13]:= {6, 0, 0, 0, 0, 0, -2, 2, 0, 0, -6}
```

```
In[14]:= tab = {Prepend[reps, " "],
      Prepend[signc, "signs"], Prepend[charp, "permut. rep."],
      Prepend[charf, "faithful rep."]; Grid[tab, Frame -> All, Background ->
      {1 -> GTBackGroundColor1, 1 -> GTBackGroundColor1, {1, 1} -> GTCornerColor},
      Dividers -> {{2 -> GTDividerColor1}, {2 -> GTDividerColor1}}]
```

	Ee	IC _{6z}	C _{3z} ⁻¹	IC _{3z}	C _{6z} ⁻¹	C _{2y}	IC _{2x}	C _{2B}	IC _{2D}	IEe	C _{2z}	IC _{2z}
signs	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
permut. rep.	6	0	0	0	0	0	0	2	2	0	0	6
faithful rep.	6	0	0	0	0	0	0	-2	2	0	0	-6

Decompose the obtained faithful representation.

```
In[15]:= GTIrep[charf, ctab];
```

$A_{2u} \oplus B_{2g} \oplus E_{1g} \oplus E_{2u}$

Figure 9.5 Construction of a faithful representation and decomposition into irreducible representations of D_{6h} .

	D_{6h}	Ee	IC _{6z}	C _{3z} ⁻¹	IC _{3z}	C _{6z} ⁻¹	C _{2y}	IC _{2x}	C _{2B}	IC _{2D}	IEe	C _{2z}	IC _{2z}
Out[8]=	A_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
	B_{2g}	1	-1	1	1	-1	1	-1	-1	1	1	-1	-1
	E_{1g}	2	1	-1	-1	1	0	0	0	0	2	-2	-2
	E_{2u}	2	1	-1	1	-1	0	0	0	0	-2	2	-2

Figure 9.6 Part of the character table of D_{6h} corresponding to the irreducible representations occurring in the decomposition given in (9.25). The classes are characterized by elements selected in Figure 9.5.

Mathematica

Construction of SALC's

```

In[8]:= GTSALC[grp_, prep_, signs_, chars_] := Module[
  {φ1, fkt, salc, cls, class, el, pos, i, k},
  φ1 = {1, 0, 0, 0, 0, 0}; fkt = Table[φ1, {i, 1, 6}];
  salc = Table[0, {6}]; cls = GTClasses[grp];
  Do[class = cls[[i]];
    Do[el = class[[k]];
      pos = Flatten[Position[grp, el]][[1]];
      salc = salc + signs[[i]] chars[[i]] prep[[pos]].φ1
      , {k, 1, Length[class]}]
    , {i, 1, Length[cls]}];
  salc = salc / Norm[salc]; Return[salc.fkt]
]

irred. representation  $A_{2u}$  (a2u contains the characters)

In[9]:= a2u = {1, -1, 1, -1, 1, -1, 1, -1, 1, -1, 1, -1};
GTSALC[d6h, prep, signc, a2u]

Out[10]=  $\frac{\phi_1}{\sqrt{6}} + \frac{\phi_2}{\sqrt{6}} + \frac{\phi_3}{\sqrt{6}} + \frac{\phi_4}{\sqrt{6}} + \frac{\phi_5}{\sqrt{6}} + \frac{\phi_6}{\sqrt{6}}$ 

irred. representation  $B_{2g}$  (b2g contains the characters)

In[11]:= b2g = {1, -1, 1, 1, -1, 1, -1, -1, 1, 1, -1, -1};
GTSALC[d6h, prep, signc, b2g]

Out[12]=  $\frac{\phi_1}{\sqrt{6}} - \frac{\phi_2}{\sqrt{6}} + \frac{\phi_3}{\sqrt{6}} - \frac{\phi_4}{\sqrt{6}} + \frac{\phi_5}{\sqrt{6}} - \frac{\phi_6}{\sqrt{6}}$ 

```

Figure 9.7 Construction of symmetry-adapted linear combinations (SALC's) for the irreducible representations A_{2u} and B_{2g} of the point group D_{6h} . The lists $a2u$, $b2g$ contain the characters of the irreducible representations.

The information about sign and position change, discussed beforehand, is used in Figure 9.7 to construct the SALC from orbital ϕ_1 (p_z -orbital at position 1 in Figure 9.4) represented by the vector $\{1, 0, 0, 0, 0, 0\}$. The SALC's are normalized assuming that localized orbitals are orthonormal. The final result is given by

$$\phi_{A_{2u}} = \frac{1}{\sqrt{6}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) , \quad (9.27)$$

$$\phi_{B_{2g}} = \frac{1}{\sqrt{6}} (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6) . \quad (9.28)$$

For the two-dimensional representations the SALC's can be constructed in a similar manner but by applying the full projection operator, as discussed for plane waves in Example 52. To apply the full projection operator the command **GT-ProjectionOperator** can be used, where the representation matrices of the two 2-dimensional representations are needed (**GTGetIrep**). Alternatively, the character projection operator can be used to construct two linear independent SALC's starting from two different orbitals, say ϕ_1 and ϕ_2 .

Task 31 (Two-dimensional representations for benzene). Construct basis functions for the irreducible representations E_{1g} and E_{2u} .

9.4
Construction of Tight-Binding Hamiltonians

Tight-binding Hamiltonians	
GTLoadStructures	Loads a structure database
GTGetStructure	Retrieves a special structure from a structure database
GTTbDatabaseInfo	Gives information about tight-binding parameter sets stored within a database
GTTbDatabaseRetrieve	Retrieves a specific tight-binding parameter set from a database
GTCluster	Generates an atomic cluster from given structural information
GTShells	Divides an atomic cluster into shells
GTPlotStructure2D	Plots a two-dimensional crystal structure
GTTbMatrixElement	Gives a matrix element in two-center form
GTSymmetryBasisFunctions	Finds basis functions associated with irreducible representations
GTGroupGlp	Estimates the group G_p^l of transformations leaving the vectors Q_p^l invariant
GTShellVectorsQlp	Finds the shell vectors Q_p^l
GTTransformQlp	Transforms shell vectors to Q_p^l
GTTbNumberOfIntegrals	Number of independent parameters in three-center form
GTTbIntegralRules	Gives rules to relate parameters to independent ones
GTTbMatrixElement3C	Gives a matrix element in three-center form
GTTbSpinOrbit	Constructs a tight-binding Hamiltonian with spin-orbit coupling
GTTbHamiltonian	Generates a tight-binding Hamiltonian in two-center form
GTTbReadWannier90	Reads information from WANNIER90 package
GTTbWannier90Hamiltonian	Constructs Hamiltonian from WANNIER90 information
GTTbParmToRule	Substitution rules for tight-binding parameters
GTHamiltonianPlot	Plots the matrix structure of a tight-binding Hamiltonian
GTHamiltonianList	Lists the analytic form of a tight-binding Hamiltonian
GTWavefunctionPlot	Gives a graphical overview of the structure of eigenvectors
GTBandStructure	Calculates and plots a band structure for a given Hamiltonian
GTDensityOfStates	Calculates the density of states for a given Hamiltonian
GTWriteToFile	Writes data, e.g., Hamiltonians, to an external file
GTReadFromFile	Reads data, e.g., Hamiltonians, from an external file

In the tight-binding approximation, the wave function $\phi_{\mathbf{k}}(\mathbf{r})$, representing the solution of the SCHRÖDINGER equation (9.1) is constructed via a linear combination of BLOCH functions $\psi_n^s(\mathbf{k}, \mathbf{r})$, built up from localized orbitals φ_n at the sites $\mathbf{t} + \mathbf{r}_s$,

as introduced within the previous section (ν – band index),

$$\phi_{\mathbf{k},\nu}(\mathbf{r}) = \sum_{s=1}^{N_s} \sum_{n=1}^{N_b^s} c_{ns}^\nu(\mathbf{k}) \psi_n^s(\mathbf{k}, \mathbf{r}), \quad \psi_n^s(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{t}} e^{i\mathbf{k}\cdot\mathbf{t}} \varphi_n(\mathbf{r} - \mathbf{t} - \mathbf{r}_s) \quad (9.29)$$

It is assumed that the crystal contains N_s sublattices, represented by the vectors $\mathbf{r}_s$. At each site corresponding to a sublattice s , a number of N_b^s atomic wave functions are used to describe the electronic structure of the atom. Analogously to equation (9.7), the ansatz (9.29) can be used to reformulate the SCHRÖDINGER equation in terms of a matrix eigenvalue problem, having the dimension $N_{\text{dim}} = \sum_{s=1}^{N_s} N_b^s$. The matrix elements of the Hamiltonian in the tight-binding basis are given by

$$\begin{aligned} H_{i,j} &= H_{n',n}^{s',s} = \left(\psi_{n'}^{s'}, H \psi_n^s \right) \\ &= \frac{1}{N} \sum_{\mathbf{t}, \mathbf{t}'} e^{i\mathbf{k}(\mathbf{t}-\mathbf{t}')} \left(\varphi_{n'}(\mathbf{r} - \mathbf{t}' - \mathbf{r}_{s'}), \hat{H} \varphi_n(\mathbf{r} - \mathbf{t} - \mathbf{r}_s) \right), \\ &= \sum_{\mathbf{t}} e^{i\mathbf{k}\cdot\mathbf{t}} \left(\varphi_{n'}(\mathbf{r} - \mathbf{r}_{s'}), \hat{H} \varphi_n(\mathbf{r} - (\mathbf{t} + \mathbf{r}_s)) \right), \\ &= \sum_{\mathbf{t}} e^{i\mathbf{k}\cdot\mathbf{t}} E_{n',n}(\mathbf{r}_{s'}; \mathbf{t} + \mathbf{r}_s), \end{aligned} \quad (9.30)$$

where the $H_{i,j}$ are characterized by a combined index (e.g., $j = (s, n)$, $s = 1, \dots, N_s$, $n = 1, \dots, N_b^s$). A coordinate transformation in the integral together with the difference $(\mathbf{t} - \mathbf{t}')$ occurring N times within the summation was used to obtain (9.30). A similar derivation as for the Hamiltonian can be applied to obtain the correct form of the overlap matrix $\underline{S}$. In summary, the following integrals have to be evaluated,

$$E_{n',n}(\mathbf{r}_{s'}, \mathbf{t} + \mathbf{r}_s) = \left(\varphi_{n'}(\mathbf{r} - \mathbf{r}_{s'}), \hat{H} \varphi_n(\mathbf{r} - (\mathbf{t} + \mathbf{r}_s)) \right), \quad (9.31)$$

$$S_{n',n}(\mathbf{r}_{s'}, \mathbf{t} + \mathbf{r}_s) = \left(\varphi_{n'}(\mathbf{r} - \mathbf{r}_{s'}), \varphi_n(\mathbf{r} - (\mathbf{t} + \mathbf{r}_s)) \right). \quad (9.32)$$

The values of $E_{n',n}$ and $S_{n',n}$ are assumed to be parameters in an empirical tight-binding scheme (ETB). Incorporating the symmetry of the system, the parameters can be reduced to a few independent ones. To obtain numerical values, tight-binding parameters can be obtained, e.g., by fitting the model Hamiltonian to an *ab initio* band structure. The basis set of atomic wave functions can be transformed by a so-called LÖWDIN transformation [122] such that the overlap matrix becomes diagonal. In ETB schemes wave functions are not used explicitly. Therefore, a diagonal overlap matrix $\underline{S}$ is commonly used.

The Hamiltonian consists of the kinetic energy term and a single-particle potential. Without approximation, the potential is written as a sum of atom-centered potentials. Thus, the Hamiltonian is given by

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \sum_{s=1}^{N_s} \sum_{\mathbf{t}} V_s(\mathbf{r} - \mathbf{t} - \mathbf{r}_s). \quad (9.33)$$

The potentials $V_s(\mathbf{r})$ and the wave functions $\varphi_n, \varphi_{n'}$ are localized at the corresponding atomic positions. A sufficiently large overlap between wave functions and potentials has to be present, to get contributions to (9.31). These contributions can be characterized with respect to the following scheme.

- The quantity is a so-called *on-site* integral if potential and wave functions are located at the same site.
- If the wave functions are at separate positions but the potential is located at one of them, it is called a *two-center* integral.
- It is a *three-center* integral if the wave functions and the potential are located at different sites.

The two-center approximation and the three-center approximation of the empirical tight-binding method will be discussed with respect to the GTPack implementation in the next sections.⁷⁾

9.4.1

Hamiltonians in Two-Center Form

First, the tight-binding method is discussed within the two-center approximation, where the wave functions are at separate positions and the potential is located at one of them. In this approximation the occurring integrals are equivalent to the ones for diatomic molecules. Therefore, it is common to express the hopping integrals $E_{n',n}$ in a chemical notation, i.e., in the so-called two-center integrals $(ss\sigma), (sp\sigma), (pp\sigma), (pp\pi), \dots$ (see Figure 9.8). The construction of the TB-Hamiltonian in two-center form consists of two steps.

1. The integrals $E_{n',n}(\tau_s; \mathbf{t} + \tau_s)$ have to be expressed in two-center form.
2. The sum over the lattice vectors (9.30) has to be evaluated.

The decomposition of the hopping integrals in two-center approximation requires the quantization of the orbitals with respect to the vector connecting the atoms. This leads to a rotation of the spherical harmonics as discussed in detail by PODOLSKIY and VOGL [125] (cf. also Appendix A). This approach is also implemented within GTPack. The command **GTTbMatrixElement** allows one to construct the expressions for angular momenta up to $l = 3$ (the method can be easily extended to higher angular momenta). The original expressions from the seminal paper of SLATER and KOSTER [126] can be reproduced nicely.

The application of **GTTbMatrixElement** is shown in Figure 9.9, where the transformation of integrals from three-center to two-center form between a p_z -orbital and the orbitals s, p_x, p_y, p_z is calculated. DL, DM, DN (denoted as l, m, n in [126]) denote the direction cosines of the vector $\mathbf{t}$ connecting the two sites. As addressed in [125], tables of integrals in the literature may contain misprints, which can be avoided easily and efficiently by using an automated construction.

7) A fourth contribution, where wave functions are at the same site, but the potential is located somewhere else, is neglected in the following (see [123, 124] for more information).

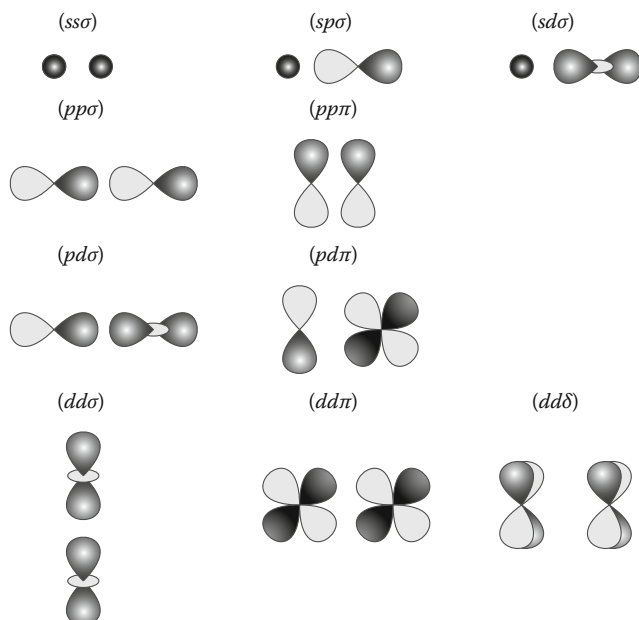


Figure 9.8 Schematic view of the different two-center integrals up to $l = 2$. Real spherical harmonics are used. Positive lobes are depicted dark and negative lobes are depicted light.

Mathematica

GTTbMatrixElement

```
In[8]:= t = {};
Do[Do[t = Append[t, {1, m, GTTbMatrixElement[1, m, 1, 0, 1]}],
  {m, -1, 1}], {1, 0, 1}];
tab = Prepend[t, {"1", "m", "E(R)"}];
Grid[tab, Frame -> All,
  Background -> {{1 -> GTBackgroundColor1, 2 -> GTBackgroundColor1},
    1 -> GTBackgroundColor1, {{1, 1}, {1, 2}} -> GTCornerRadius}]
```

1	m	E(R)
0	0	DN (spσ) ₁
1	-1	DM DN (- (ppπ) ₁ + (ppσ) ₁)
1	0	(ppπ) ₁ + DN ² (- (ppπ) ₁ + (ppσ) ₁)
1	1	DL DN (- (ppπ) ₁ + (ppσ) ₁)

Figure 9.9 Analytic decomposition of three-center integrals $E_{ij}(\mathbf{R})$ in two-center form, for the interaction of a p_z orbital with orbitals $s, p_y, p_z, p_x (m = 0, -1, 0, 1)$.

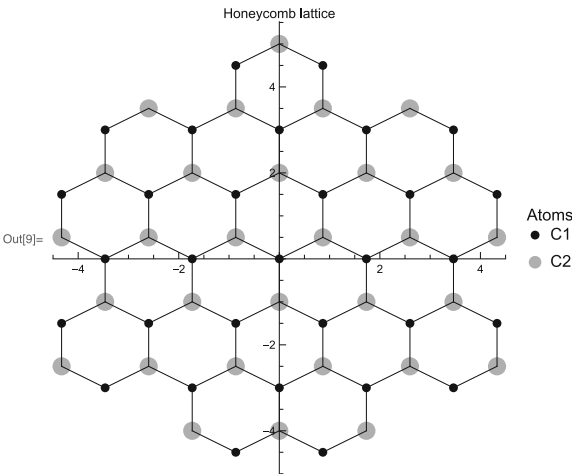
It follows from Figure 9.9 that for two p_z -orbitals

$$E_{z,z}(\mathbf{t}) = (pp\pi)_1 + n^2 [(pp\sigma)_1 - (pp\pi)_1] \quad (9.34)$$

holds. The direction cosine of $\mathbf{t}$ with respect to the z -axis is n . If both orbitals are located at the z -axis a σ -bond is formed ($n = \pm 1$). If $\mathbf{t} \perp \mathbf{e}_z$ the direction cosine n is zero. The centers of both orbitals are located in the x - y -plane and the orbitals form a π bond.

Mathematica
GTPlotStructure2D, GTCluster, GTShells, GTTbHamiltonian, GTHamiltonianPlot

```
In[8]:= hcp = {{ "C", "Honeycomb"}, "hP1", "A6", "P6/mmm",  
191, {{Sqrt[3] a, 0, 0}, {Sqrt[3] a / 2, 3 a / 2, 0}, {0, 0, 0}},  
{{{0, 0, 0}, "C1"}, {{0, -a, 0}, "C2"}}, {a -> 240}};  
  
In[9]:= GTPlotStructure2D[hcp, 5, GOLattice -> {a -> 1}, PlotLabel -> "Honeycomb lattice",  
PlotStyle -> {{Black, PointSize[Large]}, {GrayLevel[0.6], PointSize[.04]}}]  
  
61 atoms  
  
Atoms in cluster: {{C1, 31}, {C2, 30}}
```



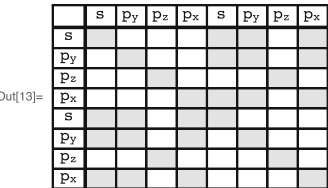
Create a cluster and reorder in shells for the Hamiltonian construction.

```
In[10]:= c1 = GTCluster[hcp, 6, GOLattice -> {a -> 1}];  
bas0 = hcp[[7]] /. {a -> 1}; shells = {2, 2};  
  
85 atoms  
  
Atoms in cluster: {{C1, 43}, {C2, 42}}  
  
In[12]:= lat = GTShells[c1, bas0, shells, GVerbose -> True,  
GOTbLattice -> {{ "C1,C1", {0}}, { "C2,C2", {0}}, { "C1,C2", {1}}},  
GOPosition -> "Relative"];
```

Basis	dist	Atoms	dist	Atoms
C1	1	{{C2, 3}}	$\sqrt{3}$	{{C1, 6}}
C2	1	{{C1, 3}}	$\sqrt{3}$	{{C2, 6}}

Construct the Hamiltonian and plot the structure.

```
In[13]:= bas = {{ "C1", 1, {0, 1}}, { "C2", 1, {0, 1}}};  
hamc = GTTbHamiltonian[bas, lat]; GTHamiltonianPlot[hamc, bas]
```



```
In[14]:= hpp = {{hamc[[3, 3]], hamc[[3, 7]]}, {hamc[[7, 3]], hamc[[7, 7]]}};
```

Figure 9.10 Construction of the tight-binding Hamiltonian for graphene.

Example 54 (Tight-binding band structure of graphene). Since it serves as a prototype for two-dimensional DIRAC materials [24], graphene is one of the most-studied materials to date [23, 127]. The wide-ranging theoretical studies on the material during the past half-century together with the uncovering of promising and interesting physics were strong enough that the first experimental realization of graphene [128] was awarded with the NOBEL Prize in Physics in 2010. However, because of its weak next nearest neighbor interactions and the 2-dimensional crystal structure it also serves as an ideal example to demonstrate the construction of tight-binding Hamiltonians within GTPack.

The construction of the two-center tight-binding Hamiltonian is shown in Figure 9.10). The structure of graphene is given by a Honeycomb lattice, which can be expressed as a triangular lattice with two atoms in the basis. The lattice information is stored in the list `hcp`, having the format used in the structure database `GTPack.struc`. The structure is plotted using `GTPlotStructure2D`. The notation “C1” and “C2” is used to distinguish the carbon atoms in the two sublattices. The command `GTCluster` allows to generate a cluster of atoms within a certain radius around the origin. The lattice constant $a = 1$ is used. The cut-off radius is set to $r_c = 6$. The cluster is reordered in shells by means of `GTShells`. The option `GOTbLattice` permits to specify which shells will be used in the Hamiltonian construction. Here, only the nearest neighbor interaction, i.e., the interaction between sort “C1” and sort “C2” is included. The list `bas` describes the basis, the species on the sublattices, and which angular momenta will be taken into account. For graphene, s - and p -orbitals are appropriate, i.e., the list of angular momenta is given by $\{0,1\}$ ⁸⁾. `GTTbHamiltonian` constructs the Hamiltonian from the information about basis and structure in an analytical form. Four orbitals per site are used. Therefore, a 8×8 Hamiltonian matrix results. `GTHamiltonianPlot` displays the structure of the Hamiltonian. Matrix elements different from zero are marked in gray. As can be verified nicely, the σ - and π -electron systems are decoupled.

Figure 9.11 demonstrates the calculation of the band structure. First, `GTBZPath` is used to generate a standard path within the BRILLOUIN zone. For the calculation only the π -electron system is taken into account, i.e., only entries associated with the p_z -electrons are considered. Doing so, a 2×2 -Hamiltonian remains. To obtain numerical values within a band structure calculation, a substitution rule is defined for the tight-binding parameters. The on-site interaction is set to 0 (i.e., the FERMIL level is defined to be zero) and the next nearest neighbor interaction is chosen to be -2 (arb. units). The band structure itself is calculated and plotted using the command `GTBandStructure`. The DIRAC crossings, i.e., linear crossings of energy bands can be nicely seen at the K and K' point within the BRILLOUIN zone. The dispersion relation of elementary excitations at these two points behave as massless DIRAC fermions.

The overlap matrix for a nonorthogonal problem has the same analytic structure as the Hamiltonian. The results obtained up to now allow to include the full

8) To take into account the d -orbitals as well, one would need to specify $\{0,1,2\}$. The setting $\{0,2\}$ would mean s and d only.

Mathematica
GTBZPath, GTBandStructure

```
In[8]:= kp = GTBZPath["Honeycomb"]
Out[8]= {{ {- 2/(3 Sqrt[3]), 0, 0}, {0, 0, 0}, {1/(2 Sqrt[3]), -1/6, 0}, {2/(3 Sqrt[3]), 0, 0}}, {K', I, M, K}}

Rule to substitute parameters in Hamiltonian.

In[9]:= hamrule = {"(pp0)"^"c1" -> 0, "(pp0)"^"c2" -> 0, "(ppp)"^"c1,c2" -> -2};
hparm = hpp /. hamrule
Out[9]= {{0, -2 (Cos[2 π η] + 2 e^(1/2 π η) Cos[Sqrt[3] π ξ] - i Sin[2 π η])},
{-2 Cos[2 π η] - 4 Cos[π η] Cos[Sqrt[3] π ξ] + i (4 Cos[Sqrt[3] π ξ] Sin[π η] - 2 Sin[2 π η]), 0}}

In[10]:= GTBandStructure[hparm, kp // N, 25, 2, Joined -> True, PlotStyle -> Black,
PlotRange -> {{0, 0.911}, {-6.2, 6.2}}, FrameLabel -> {"", "Energy (arb. units)"},
PlotLabel -> "π-electrons in Graphene"]
Maximum Abscissa = 0.910684
```

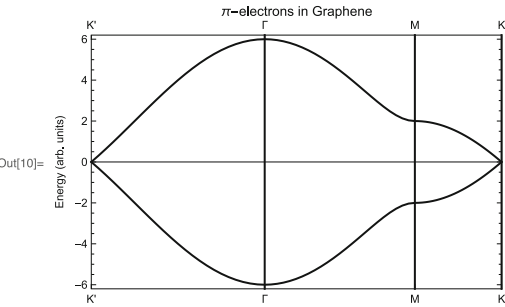


Figure 9.11 Calculation of π bands of graphene.

set of orbitals. Figure 9.12 demonstrates that two substitution rules are used to prepare both, the Hamiltonian and the overlap matrix for the calculation. The final band structure calculation in Figure 9.12 is performed using **GTBandStructure**.

Task 32 (*d*-orbitals on a square lattice). Construct the two-center tight-binding Hamiltonian for *d*-electrons on a square lattice. Nearest neighbor and next nearest neighbors have to be included. Use the parameters for Cu from the TB_Handbook.parm library. Plot the band structure. Discuss the results in relation to the band structure of Cu given in Figure 9.1.

9.4.2
Hamiltonians in Three-Center Form

The general structure of the eigenvalue problem obtained within the tight-binding approximation is given by (9.7) and (9.30) as well as (9.31) and (9.32). Tables to evaluate the matrix elements in (9.30) in two- and three-center form for cubic

Mathematica**Graphene with full basis set**

Rules to substitute parameters in Hamiltonian and overlap matrix.

```
In[8]:= overlap = { "(ss0)" "c1" → 1, "(ss0)" "c2" → 1,
  "(pp0)" "c1" → 1, "(pp0)" "c2" → 1, "(ssσ)" "1" "c1,c2" → 0.212,
  "(spσ)" "1" "c1,c2" → -0.102, "(psσ)" "1" "c1,c2" → -0.102, "(ppσ)" "1" "c1,c2" → -0.146,
  "(ppπ)" "1" "c1,c2" → 0.1290};

In[9]:= hopping = { "(ss0)" "c1" → -8.868, "(ss0)" "c2" → -8.868,
  "(pp0)" "c1" → 0, "(pp0)" "c2" → 0, "(ssσ)" "1" "c1,c2" → -6.769,
  "(spσ)" "1" "c1,c2" → 5.580, "(psσ)" "1" "c1,c2" → 5.580, "(ppσ)" "1" "c1,c2" → 5.037,
  "(ppπ)" "1" "c1,c2" → -3.033};

In[10]:= over = hamc /. overlap; hopp = hamc /. hopping;

In[11]:= bnds = GTBandStructure[{hopp, over}, kp // N, 100, 8,
  GOTbOrthogonal → False, Joined → True, PlotRange → {{0, 0.911}, {-20, 35}},
  FrameLabel → {"", "Energy (arb. units)"}, PlotStyle → Black,
  PlotLabel → "Electronic structure of Graphene"]

Maximum Abscissa = 0.910684
```

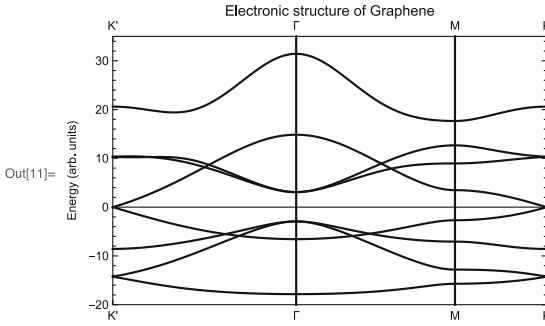


Figure 9.12 Calculation of the complete band structure of graphene. Parameters are taken from MIN *et al.* [129].

structures including s -, p -, and d -electrons were communicated by SLATER and KOSTER [126]. In general, an extension to f -electrons or complex crystal structures becomes tedious. A method to construct tight-binding Hamiltonians in three-center form was developed by EGOROV *et al.* [130]. To date, the method is partially implemented in GTPack and will be discussed subsequently. In the following, the method is introduced for the example of a simple cubic structure with one atom per cell (point group O_h)⁹⁾.

In contrast to the ansatz for the two-center formalism in equation (9.29), BLOCH functions are now constructed from symmetrized localized atomic functions, transforming as the μ th row of the irreducible representation Γ^j of the point

9) Besides brevity, this allows a comparison with the table in [126].

group $\mathcal{G}_0^{(10)11)}$

$$\psi_{\mu}^{js}(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{t}} e^{i\mathbf{k} \cdot (\mathbf{t} + \mathbf{r}_s)} \hat{P}(T_{\mathbf{T}}) \varphi_{\mu}^j(\mathbf{r}). \quad (9.35)$$

Real linear combinations of spherical harmonics in Cartesian coordinates are used as angular parts of the atomic functions. The GTPack command **GTSymmetryBasisFunctions** is used to associate the spherical harmonics to the irreducible representations of $\mathcal{G}_0$. Considering the simple-cubic case and the point group O_h it follows

$$s: \quad \Gamma_1 \quad (9.36)$$

$$p(x, y, z): \quad \Gamma_{15} \quad (9.37)$$

$$e_g(3z^2 - r^2, x^2 - y^2): \quad \Gamma_{12} \quad (9.38)$$

$$t_{2g}(xy, xz, yz): \quad \Gamma_{25'} \quad (9.39)$$

Within the calculation of the matrix elements of the Hamiltonian, the nonprimitive vector $\mathbf{r}_s$ denotes the position of a site belonging to the sublattice s within the unit cell. It can be expressed in terms of the translation operator

$$T_{\mathbf{T}} = \{\underline{1} \mid \mathbf{t} + \mathbf{r}_s\}. \quad (9.40)$$

The matrix elements of the Hamiltonian are

$$H_{\mu', \mu}^{j's', js}(\mathbf{k}) = \left(\psi_{\mu'}^{j's'}, \hat{H} \psi_{\mu}^{js} \right) = e^{i\mathbf{k} \cdot (\mathbf{r}_s - \mathbf{r}_{s'})} \sum_{\mathbf{t}} e^{i\mathbf{k} \cdot \mathbf{t}} E_{\mu', \mu}^{j', j}(\mathbf{r}_{s'}; \mathbf{t} + \mathbf{r}_s), \quad (9.41)$$

where the energy integrals are given by

$$\begin{aligned} E_{\mu', \mu}^{j', j}(\mathbf{r}_{s'}; \mathbf{t} + \mathbf{r}_s) &= \int \hat{P}(\{\underline{1} \mid \mathbf{r}_{s'}\}) \varphi_{\mu'}^{j'\star}(\mathbf{r}) \hat{H} \hat{P}(\{\underline{1} \mid \mathbf{t} + \mathbf{r}_s\}) \varphi_{\mu}^j(\mathbf{r}) d^3\mathbf{r}, \\ &= \int \varphi_{\mu'}^{j'\star}(\mathbf{r} - \mathbf{r}_{s'}) \hat{H} \varphi_{\mu}^j(\mathbf{r} - \mathbf{t} - \mathbf{r}_s) d^3\mathbf{r}. \end{aligned} \quad (9.42)$$

Starting point of the analysis are the Hermiticity and the symmetry properties of $\hat{H}$. As a consequence of the Hamiltonian being Hermitian, the matrix elements and energy integrals have to fulfill the relations

$$H_{\mu', \mu}^{j's', js}(\mathbf{k}) = H_{\mu, \mu'}^{js, j's'}(\mathbf{k})^*, \quad (9.43)$$

$$E_{\mu', \mu}^{j', j}(\mathbf{r}_{s'}; \mathbf{t} + \mathbf{r}_s) = E_{\mu, \mu'}^{j, j'}(\mathbf{r}_s; -\mathbf{t} + \mathbf{r}_{s'})^*. \quad (9.44)$$

A special property of the energy integral follows, if the group of the SCHRÖDINGER equation contains symmetry elements like $\{\underline{1} \mid \mathbf{r}\}$. Then, by using

$$\{\underline{1} \mid \mathbf{r}\} \{\underline{1} \mid \mathbf{r}_s\} = \{\underline{1} \mid \mathbf{r} - \mathbf{r}_s\} = \{\underline{1} \mid \mathbf{r} - \mathbf{r}_s\} \{\underline{1} \mid 0\}$$

10) The constant phase factor $\exp(i\mathbf{k} \cdot \mathbf{r}_s)$ is taken into account explicitly.

11) Symmorphic space groups are considered.

the following relation can be obtained from (9.42),

$$E_{\mu',\mu}^{j',j}(\mathbf{r}_{s'}; \mathbf{t} + \mathbf{r}_s) = \omega^{j'} \omega^j E_{\mu',\mu}^{j',j}(\mathbf{r} - \mathbf{r}_{s'}; -\mathbf{t} + \mathbf{r} - \mathbf{r}_s). \quad (9.45)$$

The Hamiltonian is invariant under all symmetry operations of the group of the SCHRÖDINGER equation. Thus, the Hamiltonian commutes with each of these symmetry operations and the eigenfunctions of the Hamiltonian are also eigenfunctions of the symmetry operations. Atomic basis functions are eigenfunctions of the inversion or parity operator $\hat{I}$. The parity eigenvalues are denoted by ω^j ,

$$\hat{I} \varphi_{\mu}^j(\mathbf{r}) = \omega^j \varphi_{\mu}^j(\mathbf{r}), \quad \omega^j = \pm 1. \quad (9.46)$$

Atomic s and d functions have even parity ($\omega^j = +1$), whereas p functions are functions with odd parity ($\omega^j = -1$).

Additional relations can be found by incorporating the point group symmetry. Let the rotation $T_R = \{\underline{\mathbf{R}} | 0\}$ be an element of the point group $\mathcal{G}_0$. The combination with a translation $T_T = \{\underline{\mathbf{1}} | \mathbf{t}\}$ leads to

$$T_R T_T = \{\underline{\mathbf{R}} | 0\} \{\underline{\mathbf{1}} | \mathbf{t}\} = \{\underline{\mathbf{R}} | \underline{\mathbf{R}}\mathbf{t}\} = \{\underline{\mathbf{1}} | \underline{\mathbf{R}}\mathbf{t}\} \{\underline{\mathbf{R}} | 0\}. \quad (9.47)$$

The operation $T_R \in \mathcal{G}_0$ commutes with $\hat{H}$ which gives rise to

$$\begin{aligned} E_{\mu',\mu}^{j',j}(\mathbf{r}_{s'}; \mathbf{t} + \mathbf{r}_s) = \\ \int \left[\hat{P}(\{\underline{\mathbf{1}} | \underline{\mathbf{R}}\mathbf{r}_{s'}\}) \hat{P}(T_R) \varphi_{\mu'}^{j'}(\mathbf{r}) \right]^* \hat{H} \hat{P}(\{\underline{\mathbf{1}} | \underline{\mathbf{R}}(\mathbf{t} + \mathbf{r}_{s'})\}) \hat{P}(T_R) \varphi_{\mu}^{j'}(\mathbf{r}) d^3\mathbf{r}. \end{aligned} \quad (9.48)$$

Since $\varphi_{\mu'}^{j'}(\mathbf{r})$ and $\varphi_{\mu}^j(\mathbf{r})$ are basis functions of the irreducible representations $\Gamma^{j'}$ and Γ^j , they transform as

$$\hat{P}(T_R) \varphi_{\mu}^j(\mathbf{r}) = \sum_{\nu} \Gamma_{\nu\mu}^j(T_R) \varphi_{\nu}^j(\mathbf{r}). \quad (9.49)$$

Therefore, equation (9.48) leads to

$$E_{\mu',\mu}^{j',j}(\mathbf{r}_{s'}; \mathbf{t} + \mathbf{r}_s) = \sum_{\nu',\nu} \Gamma_{\nu'\mu'}^{j'}(T_R)^* \Gamma_{\nu\mu}^j(T_R) E_{\nu',\nu}^{j',j}(\underline{\mathbf{R}}\mathbf{r}_{s'}; \underline{\mathbf{R}}(\mathbf{t} + \mathbf{r}_s)). \quad (9.50)$$

The lattice sum in the construction of the matrix elements can be split into a sum over coordination spheres (shells) S_p and a sum over all vectors in the corresponding coordination sphere. **GTcluster** and **GTshells** are used to generate a cluster of atoms and sort it into shells. Three shells in correspondence with [126] will be taken into account. All vectors within a shell are connected by symmetry elements of the point group $\mathcal{G}_0$. Therefore, a minimal set of vectors $\mathbf{Q}_p^l$ from each coordination sphere S_p can be selected to represent all vectors,

$$\{\underline{\mathbf{R}} | 0\}(\mathbf{t} + \mathbf{r}_s) = \mathbf{Q}_p^l, \quad \{\underline{\mathbf{R}} | 0\} \in \mathcal{G}_0. \quad (9.51)$$

The GTPack command **GTShellVectorsQlp** can be used to determine these vectors. For the simple cubic structure, one vector per shell remains to be taken into account,

$$\mathbf{Q}_1^1 = (1, 0, 0)a, \quad (9.52)$$

$$\mathbf{Q}_2^1 = (1, 1, 0)a, \quad (9.53)$$

$$\mathbf{Q}_3^1 = (1, 1, 1)a. \quad (9.54)$$

All operations of G_0 , leaving the vector $\mathbf{Q}_p^1$ invariant form a subgroup, denoted by G_p^1 . The groups G_p^1 together with their generators can be found by **GTGroupGlp**. The generators for the sc structure are

$$G_1^1: \{IC_{2e}, C_{4x}\}, \quad (9.55)$$

$$G_2^1: \{C_{2a}, IC_{2z}\}, \quad (9.56)$$

$$G_3^1: \{C_{3\delta}, IC_{2b}\}. \quad (9.57)$$

Using the character tables of the groups G_p^1 the following coefficients c_i^j are introduced,

$$c_i^j = \frac{1}{g} \sum_{\alpha \in G_p^1} \chi^{j*}(\alpha) \chi^i(\alpha), \quad (9.58)$$

where g is the order of G_p^1 and $\chi^j(\alpha)$ are the characters of the j th irreducible representation of G_0 corresponding to the basis functions, i.e., $\Gamma_1, \Gamma_{15}, \Gamma_{12}, \Gamma_{25'}$ in the present case. The $\chi^i(\alpha)$ correspond to the i th irreducible representation of G_p^1 . The energy integrals (9.42) appearing in a certain Hamiltonian are not independent from each other. Therefore, it is important to find the minimal set of energy integrals that represent the problem. Using the coefficients c_i^j from (9.58) the numbers of independent parameters are found by

$$N_{jj'} = \begin{cases} \sum_i c_i^j c_i^{j'} & \text{for } j \neq j', \\ \sum_i c_i^j (c_i^j + 1) & \text{for } j = j'. \end{cases} \quad (9.59)$$

To calculate $N_{jj'}$ within GTPack, **GTTbNumberOfIntegrals** is used. Figure 9.13 presents the results for the sc structure.

1/1	s	p	d _{eg}	d _{t2g}
s	1	1	1	0
p	1	2	1	1
d _{eg}	1	1	2	0
d _{t2g}	0	1	0	2

(a)

2/1	s	p	d _{eg}	d _{t2g}
s	1	1	1	1
p	1	3	2	2
d _{eg}	1	2	2	1
d _{t2g}	1	2	1	3

(b)

3/1	s	p	d _{eg}	d _{t2g}
s	1	1	0	1
p	1	2	1	2
d _{eg}	0	1	1	1
d _{t2g}	1	2	1	2

(c)

Figure 9.13 Number of independent parameters for the first three shells in a three-center tight-binding Hamiltonian for a simple-cubic structure and a *spd*-basis. (a) First shell; (b) second shell; (c) third shell.

Using (9.51) the matrix element (9.41) can be reformulated to

$$H_{\mu',\mu}^{j's',js}(\mathbf{k}) = e^{-i\mathbf{k}\cdot\mathbf{r}_{s'}} \sum_p \sum_l \sum_{T_R \in S_p} e^{i\mathbf{R}\mathbf{k}\cdot\mathbf{Q}_p^l} E_{\mu',\mu}^{j'j}(\mathbf{r}_{s'}; \mathbf{R}^{-1}\mathbf{Q}_p^l), \quad (9.60)$$

where the sum runs over all coordination spheres and the nonequivalent vectors $\mathbf{Q}_p^l$ of the coordination sphere. If the coordinate system is chosen such that $\mathbf{r}_{s'} = 0$, the Hamiltonian matrix element has the simple form¹²⁾

$$H_{\mu',\mu}^{j's',js}(\mathbf{k}) = \sum_p \sum_l \sum_{v',v} E_{\mu',\mu}^{j',j}(\mathbf{Q}_p^l) \left[\sum_{T_R \in S_p} e^{i\mathbf{R}\mathbf{k}\cdot\mathbf{Q}_p^l} \Gamma_{v',\mu'}^{j'}(T_R)^* \Gamma_{v,\mu}^j(T_R) \right]. \quad (9.61)$$

Equation (9.61) is a central part of the method. The bracket defines the dependence on $\mathbf{k}$, i.e., the angular part of the matrix elements.

Furthermore, it follows from (9.50) that energy integrals for a fixed vector $\mathbf{Q}_p^l$ are related by

$$E_{\mu',\mu}^{j',j}(\mathbf{Q}_p^l) = \sum_{v,v'} \Gamma_{v',\mu'}^{j'}(T_R)^* \Gamma_{v,\mu}^j(T_R) E_{v',v}^{j',j}(\mathbf{Q}_p^l). \quad (9.62)$$

Equation (9.62) is used to reduce the number of energy integrals. The method is shown in Figures 9.14 and 9.15.

In Figure 9.14 the contribution of the first neighbor shell in a simple cubic structure to the diagonal element (x/x) of the $p-p$ block is calculated. The representation matrices of the generators of $\mathcal{G}_1^1$ are needed, which can be estimated using **GTGetrepMatrix**. The representation matrices are used to find relations between the energy integrals, according to (9.62). To do so, **GTTbIntegralRules** is applied, to solve a system of equations resulting in a list of relations. The first sublist reveals that a series of energy integrals are zero and that I33 and I22 are equivalent. The second sublist contains the independent energy integrals.¹³⁾ All together two independent energy integrals (I11, I22) occur in the expressions for first-shell contributions to the $p-p$ block of the Hamiltonian. This is in accordance with Figure 9.13a. **GTVarList** translates the information into a form usable for the construction of Hamiltonian matrix elements. Afterwards, the representation matrices of the symmetry elements transforming the shell vectors to $\mathbf{Q}_1^1$ have to be known. The vectors are found during a preliminary calculation using **GTTTransformToQlp**, where the outcome is stored within the list *trafo*. **GTTbMatrixElement3C** reveals the matrix element in three-center form. It is expressed in the two energy integrals I11 and I22. In a last step, the symbolic forms are substituted by a notation used by SLATER and KOSTER [126]. Figure 9.15 reveals the results for the second and third shell. The algorithm is the same, but the correct generators of the groups $\mathcal{G}_p^l$ and the corresponding set of transformations to $\mathbf{Q}_p^l$ have to be used.

12) $E_{\mu',\mu}^{j',j}(0; \mathbf{Q}_p^l) = E_{\mu',\mu}^{j',j}(\mathbf{Q}_p^l)$ is used.

13) $I\mu'\mu$ is used as a symbolic name corresponding to $E_{\mu',\mu}^{j',j}$. It is not necessary to indicate j', j during this step of consideration.

Mathematica**GTTbIntegralRules, GTTbSymbol3C, GTTbMatrixElement3C****First shell**

Representation matrices of generators of $\mathcal{G}_1^1$ for representation Γ_{15} (p -orbitals) from list G15.

```
In[8]:= p0 = GTGetIrepMatrix[group, G15, {IC2e, C4x}, GOverbose -> True]
```

IC _{2e}	C _{4x}
$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}$

```
Out[8]:= {{IC2e, {{1, 0, 0}, {0, 0, -1}, {0, -1, 0}}}, {C4x, {{1, 0, 0}, {0, 0, 1}, {0, -1, 0}}}}
```

Relations between the three-center integrals.

```
In[9]:= {rule, list} = GTTbIntegralRules[p0, p0, GOverbose -> False]
varpp = GTTbVarList[3, 3, rule]
```

```
Out[9]:= {{{I12 -> 0, I13 -> 0, I21 -> 0, I23 -> 0, I31 -> 0, I32 -> 0, I33 -> I22}}, {I11}}
```

```
Out[10]:= {{{I11, I21, I31, I12, I22, I32, I13, I23, I33}, {I11, 0, 0, 0, I22, 0, 0, 0, I22},
{1, 2, 3, 1, 2, 3, 1, 2, 3}, {1, 1, 1, 2, 2, 2, 3, 3, 3}}}
```

Transformations to the shell vector Q_1^1 and corresponding representation matrices

```
In[11]:= trf = trafo[[1, 1]];
pt = GTGetIrepMatrix[group, G15, trf, GOverbose -> True];
```

C _{2b}	C _{2z}	C _{2d}	C _{2c}	E _e	C _{2a}
$\begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

Calculate the matrix element.

```
In[13]:= mat = GTTbMatrixElement3C[pt, pt, 1, 1, varpp, {1, 0, 0}, {ξ, η, ζ}]
```

```
Out[13]:= 2 I22 (Cos[ξ] + Cos[η]) + 2 I11 Cos[ξ]
```

Generate symbols in standard form and substitution rules.

```
In[14]:= {symb, rule1} = GTTbSymbol3C[9, 1, 9, 1, {1, 0, 0}];
{symb, rule2} = GTTbSymbol3C[9, 2, 9, 2, {1, 0, 0}];
```

```
In[16]:= mat /. {rule1, rule2}
```

```
Out[16]:= 2 Cos[ξ] E(100)x,x + 2 (Cos[ξ] + Cos[η]) E(100)z,z
```

Figure 9.14 Construction of a three-center Hamiltonian, simple cubic structure, first neighbor shell.

Figure 9.13b,c give three independent energy integrals for the second and two independent parameters for the third shell concerning the p - p interaction. Two of the second shell parameters appear in the diagonal elements like (x/x) . The third describes the second shell contribution to (x/y) . To describe the third shell, one parameter per shell is necessary. The final matrix elements are given by¹⁴⁾

$$\begin{aligned}
 (x/x) = & 2E_{xx}(100) \cos \xi + 2E_{zz}(100) (\cos \eta + \cos \zeta) \\
 & + 4E_{xx}(110) (\cos \xi \cos \eta + \cos \xi \cos \zeta) + 4E_{yy}(110) \cos \xi \cos \eta \\
 & + 8E_{xx}(111) \cos \xi \cos \eta \cos \zeta
 \end{aligned} \tag{9.63}$$

14) Without the on-site term and notation slightly changed with respect to [126].

Mathematica**GTTbIntegralRules, GTTbSymbol3C, GTTbMatrixElement3C****Second shell**

```

In[8]:= p0 = GTGetIrepMatrix[group, G15, {IC2z, C2a}, GOverbose -> False];

In[9]:= {rule, list} = GTTbIntegralRules[p0, p0, GOverbose -> False];
varpp = GTTbVarList[3, 3, rule];

In[11]:= trf = trafo[[2, 1]];
pt = GTGetIrepMatrix[group, G15, trf, GOverbose -> False];

In[13]:= mat = GTTbMatrixElement3C[pt, pt, 1, 1, varpp, {1, 1, 0}, {ξ, η, ζ}]
Out[13]:= 4 I33 Cos[ξ] Cos[η] + 4 I11 (Cos[ξ] + Cos[η]) Cos[ξ]

In[14]:= {symp, rule1} = GTTbSymbol3C[9, 1, 9, 1, {1, 1, 0}];
{symp, rule2} = GTTbSymbol3C[9, 3, 9, 3, {1, 1, 0}];

In[16]:= mat /. {rule1, rule2}
Out[16]:= 4 (Cos[ξ] + Cos[η]) Cos[ξ] E(110)x,x + 4 Cos[ξ] Cos[η] E(110)y,y

```

Third shell

```

In[17]:= p0 = GTGetIrepMatrix[group, G15, {IC2b, C3δ}, GOverbose -> False];

In[18]:= {rule, list} = GTTbIntegralRules[p0, p0, GOverbose -> False];
varpp = GTTbVarList[3, 3, rule];

In[20]:= trf = trafo[[3, 1]];
pt = GTGetIrepMatrix[group, G15, trf, GOverbose -> False];

In[22]:= mat = GTTbMatrixElement3C[pt, pt, 1, 1, varpp, {1, 1, 1}, {ξ, η, ζ}]
Out[22]:= 8 I11 Cos[ξ] Cos[η] Cos[ξ]

In[23]:= {symp, rule1} = GTTbSymbol3C[9, 1, 9, 1, {1, 1, 1}];

In[24]:= mat /. rule1
Out[24]:= 8 Cos[ξ] Cos[η] Cos[ξ] E(111)x,x

```

Figure 9.15 Construction of a three-center Hamiltonian, simple cubic structure second and third neighbor shells.

Comparing the result, with Table II of [126],

$$\begin{aligned}
 (x/x) = & 2E_{xx}(100) \cos \xi + 2E_{yy}(100) (\cos \eta + \cos \zeta) \\
 & + 4E_{xx}(110) (\cos \xi \cos \eta + \cos \xi \cos \zeta) + 4E_{xx}(011) \cos \xi \cos \eta \\
 & + 8E_{xx}(111) \cos \xi \cos \eta \cos \zeta,
 \end{aligned} \tag{9.64}$$

it can be verified that the formulas differ in details concerning the energy integrals. This is due to the fact that the choice of the independent energy integrals per shell is not unique. From Figure 9.15, it follows that I22 ($E_{zz}(100)$) and I33 ($E_{yy}(100)$) are equivalent, i.e., (9.63) and (9.64) agree for the first shell. Another deviation

appears in the part of the second shell. The two matrix elements are equivalent if

$$E_{yy}(110) = E_{xx}(011) \quad (9.65)$$

holds. In the algorithm presented here, relations between energy integrals to the **same** vector $\mathbf{Q}_p^l$ are analyzed to minimize their number. In [126], different vectors of a neighborhood shell are also used. Equation (9.50) can be used to proof (9.65), i.e., (9.63) and (9.64) are equivalent.

The command **GTTbHamiltonian3C** summarizes all the steps to construct parts of a Hamiltonian resulting from basis functions to two irreducible representations Γ^j and $\Gamma^{j'}$ and also allows for the construction of a full Hamiltonian. However, the discussion in this chapter demonstrates that the algorithm does not work as straight forwardly as a similar method for the two-center Hamiltonians.

9.4.3

Inclusion of Spin–Orbit Interaction

In systems containing heavy elements, such as the $4d$ and $5d$ transition metals, relativistic effects cannot be neglected anymore. Relativistic corrections up to order $(1/c)^2$ are the DARWIN term, the mass-velocity correction, and the spin–orbit interaction. In the following, only the spin orbit-interaction will be discussed, since the other two relativistic corrections are hidden within the parameters of the TB-Hamiltonian, and can be incorporated, e.g., by fitting to a relativistic *ab initio* band structure. The total TB-Hamiltonian in matrix form becomes

$$\underline{\underline{H}} = \begin{pmatrix} \underline{\underline{H}}_{\text{TB}}^\uparrow & 0 \\ 0 & \underline{\underline{H}}_{\text{TB}}^\downarrow \end{pmatrix} + \underline{\underline{H}}_{\text{SO}}, \quad (9.66)$$

where the Hamiltonian $\underline{\underline{H}}_{\text{TB}}$ without spin is doubled to represent the spin-up and spin-down channels. The matrix $\underline{\underline{H}}_{\text{SO}}$ couples both spin channels and is constructed from the spin–orbit operator

$$\hat{H}_{\text{SO}} = \xi \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{\xi}{2} (\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2). \quad (9.67)$$

The quantity ξ characterizes the strength of the spin–orbit coupling and is included in the method as an additional parameter. Additionally, the spin–orbit interaction differs for different angular-momentum channels. For $4d$ - or $5d$ -transition metals the d -electrons are the main source of SOC, whereas for semiconductors such as GaAs the p -electrons have to be considered.

In the following, the construction of $\underline{\underline{H}}_{\text{SO}}$ will be discussed using the example of p -electrons. The angular parts of the basis functions in $\underline{\underline{H}}_{\text{TB}}$ are represented by real spherical harmonics S_l^m .¹⁵⁾ This basis has to be extended accordingly to

15) See Appendix A for a detailed discussion of the forms of spherical harmonics used in this text.

represent spin-up and spin-down contributions. The spin-angular functions for p -electrons and spin-up are:

$$\begin{aligned} p_x^\dagger &= S_1^\dagger \chi^+ = \frac{1}{\sqrt{2}} (Y_1^{-1} - Y_1^1) \chi^+, \\ p_y^\dagger &= S_1^\dagger \chi^+ = \frac{i}{\sqrt{2}} (Y_1^{-1} + Y_1^1) \chi^+, \quad p_z^\dagger = Y_1^0, \end{aligned} \quad (9.68)$$

where $\chi^\pm$ are the spin eigenfunctions. The corresponding spin-down functions are constructed analogously. To evaluate matrix elements of $\hat{H}_{\text{SO}}$ using this basis, the basis functions have to be expressed in terms of eigenfunctions Φ_{j,m_j} of the total angular momentum. This is done by the usual CLEBSCH–GORDON algebra. For the spin-up functions of (9.68) the relations are:

$$\begin{aligned} p_x^\dagger &= \frac{1}{\sqrt{2}} \left(-\Phi_{\frac{3}{2},\frac{3}{2}} + \frac{1}{\sqrt{3}} \Phi_{\frac{3}{2},-\frac{1}{2}} - \sqrt{\frac{2}{3}} \Phi_{\frac{1}{2},-\frac{1}{2}} \right), \\ p_y^\dagger &= \frac{i}{\sqrt{2}} \left(\Phi_{\frac{3}{2},\frac{3}{2}} + \frac{1}{\sqrt{3}} \Phi_{\frac{3}{2},-\frac{1}{2}} - \sqrt{\frac{2}{3}} \Phi_{\frac{1}{2},-\frac{1}{2}} \right), \\ p_z^\dagger &= \left(\sqrt{\frac{2}{3}} \Phi_{\frac{3}{2},\frac{1}{2}} - \frac{1}{\sqrt{3}} \Phi_{\frac{1}{2},\frac{1}{2}} \right). \end{aligned} \quad (9.69)$$

By means of relations (9.69) and the similar expressions for the spin-down channel, all matrix elements of $\hat{H}_{\text{SO}}$ are found. Finally, the matrix for p -electrons is given by

$$\underline{\underline{H}}_{\text{SO}} = \left(\begin{array}{ccc|ccc} 0 & 0 & i/2 & 0 & -i/2 & 0 \\ 0 & 0 & 0 & i/2 & 0 & -1/2 \\ -i/2 & 0 & 0 & 0 & 1/2 & 0 \\ \hline 0 & -i/2 & 0 & 0 & 0 & -i/2 \\ i/2 & 0 & 1/2 & 0 & 0 & 0 \\ 0 & -1/2 & 0 & i/2 & 0 & 0 \end{array} \right) \quad (9.70)$$

The form of the matrix corresponds to the following order of functions: $p_y^\dagger, p_z^\dagger, p_x^\dagger, p_y^\downarrow, p_z^\downarrow, p_x^\downarrow$. General formulas to build the matrices for other l -values are easily developed and given in [125]. **GTTbSpinMatrix** prepares the blocks of (9.70). **GT-TbSpinOrbit** constructs the full TB-Hamiltonian with spin–orbit coupling (9.66), where the z -axis is used as the quantization axis of spin. Applications, like the band structures of gold (see Section 9.6) and GaAs (see Section 9.7.4), are given later on.

9.4.4

Tight-Binding Hamiltonians from *ab initio* Calculations

The empirical tight-binding scheme discussed so far constructs BLOCH functions from a set of localized atomic functions. Integrals containing such functions are

understood as adjustable parameters within the method. Therefore, the explicit form of the basis functions does not matter.

A direct connection of Hamiltonians, formulated in terms of localized functions to different *ab initio* methods, is established by means of the WANNIER transformation [131]. This transformation converts BLOCH functions into localized functions. The WANNIER function from band ν at lattice point $\mathbf{t}$ in the unit cell is found from the corresponding BLOCH function $\psi_\nu(\mathbf{k}, \mathbf{r})$ by means of¹⁶⁾

$$\varphi_\nu(\mathbf{r} - \mathbf{t}) = \frac{\Omega}{(2\pi)^3} \int_{BZ} e^{-i\mathbf{k}\cdot\mathbf{t}} \psi_\nu(\mathbf{k}, \mathbf{r}) d^3\mathbf{k}. \quad (9.71)$$

Vice versa, the BLOCH function is reconstructed from the WANNIER functions via

$$\psi_\nu(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{t}} e^{i\mathbf{k}\cdot\mathbf{t}} \varphi_\nu(\mathbf{r} - \mathbf{t}). \quad (9.72)$$

The orthonormality of the WANNIER function follows from the orthonormality of the BLOCH waves

$$\int \varphi_\nu^*(\mathbf{r} - \mathbf{t}) \varphi_\mu(\mathbf{r} - \mathbf{t}') d^3\mathbf{r} = \delta_{\nu,\mu} \delta_{\mathbf{t},\mathbf{t}'} . \quad (9.73)$$

Basically due to a gauge freedom in the definition of the BLOCH waves, the definition of WANNIER functions is not unique. A phase change in the BLOCH function

$$\tilde{\psi}(\mathbf{k}, \mathbf{r}) = e^{i\chi(\mathbf{k})} \psi(\mathbf{k}, \mathbf{r}) \quad (9.74)$$

($\chi(\mathbf{k})$ – real function periodic in $\mathbf{k}$ -space) will not change the physical properties of the system, but different gauge functions lead to sets of WANNIER functions having different spreads and shapes.

The development of maximally localized WANNIER functions¹⁷⁾ turns the use of WANNIER functions into a practical scheme and the package WANNIER90 [134] is used to transform results of *ab initio* codes into WANNIER form. Although, WANNIER90 offers a lot of features (band structures, density of states, FERMI surfaces etc.), GTPack allows one to import the Hamiltonian matrix elements in WANNIER basis by means of **GTTbReadWannier90**. The Hamiltonian for an arbitrary $\mathbf{k}$ point is constructed by **GTTbWannier90Hamiltonian**. The structure of the Hamiltonian is the same as in the empirical tight-binding scheme, i.e., tools to calculate the band structure and density of states can be used in the same way. GTPack and WANNIER90 input serve as a basis for the development of model Hamiltonians with *Mathematica*.

16) Ω – unit cell volume.

17) See [132, 133] for details.

9.5

Hamiltonians Based on Plane Waves

Tight-binding Hamiltonians	
GTPwDatabaseInfo	Gives information about plane wave parameter sets stored within a database
GTPwDatabaseRetrieve	Retrieves a specific plane wave parameter set from a database
GTPwDatabaseUpdate	Adds a new plane wave parameter set to a database
GTPwPrintParmSet	Prints information from a specific plane wave parameter set
GTPwHamiltonian	Generates a pseudopotential Hamiltonian

Within the tight-binding method BLOCH functions are constructed from atomic wave functions, localized at the atom's positions. The pseudopotential method starts from a different perspective. All the electrons of an atom in a crystal can be divided into two groups: the core electrons and the valence electrons. For example, in case of Si ($1s^2 2s^2 2p^6 3s^2 3p^2$) all electrons up to the $2p$ level are considered to be core electrons. They are well localized and do not contribute to the chemical bonding in the solid. The partially filled $3s$ and $3p$ levels, however, are the basis of the formation of sp^3 hybrid orbitals, which form the tetrahedral arrangement of bonds in Si. The charge of the nucleus is screened by the charge of the core electrons. The wave functions of valence electrons are well represented by a set of plane waves. Furthermore, the screened potential can be substituted by a so-called *pseudopotential*. This leads to a smooth behavior of the *pseudo-wave function* in the core region and the correct form outside the core region. Details of the method can be found in [135–138] and a series of articles [139–141], which were used for the implementation of the method into GTPack.

Using a linear combination of plane waves (9.13) in (9.7) gives

$$\sum_{\mathbf{G}} c_{\mathbf{G}}(\mathbf{k}) \left\{ \left(\phi_{\mathbf{G}'}(\mathbf{k}, \mathbf{r}), \hat{H} \phi_{\mathbf{G}}(\mathbf{k}, \mathbf{r}) \right) - E(\mathbf{k}) \left(\phi_{\mathbf{G}'}(\mathbf{k}, \mathbf{r}), \phi_{\mathbf{G}}(\mathbf{k}, \mathbf{r}) \right) \right\} = 0, \quad (9.75)$$

$$\underline{\mathbf{H}}(\mathbf{k}) \mathbf{c}(\mathbf{k}) = E(\mathbf{k}) \underline{\mathbf{S}}(\mathbf{k}) \mathbf{c}(\mathbf{k}).$$

The dimension of the eigenvalue problem (9.75) depends on the number of plane waves taken into account. The matrix elements of $\underline{\mathbf{H}}$ and $\underline{\mathbf{S}}$ are given by

$$H_{\mathbf{G}', \mathbf{G}} = -\frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G}', \mathbf{G}} + (\phi_{\mathbf{G}'}, V(\mathbf{r}) \phi_{\mathbf{G}}) \quad (9.76)$$

and

$$S_{\mathbf{G}', \mathbf{G}} = \delta_{\mathbf{G}', \mathbf{G}}, \quad (9.77)$$

respectively. The unit cell consists of N_b atoms located at the positions $\mathbf{r}_s$. The crystal potential is a superposition of the pseudopotentials at the atomic sites

$$V(\mathbf{r}) = \sum_{\mathbf{t}} \sum_{s=1}^{N_b} V_s(\mathbf{r} + \mathbf{t} + \mathbf{r}_s). \quad (9.78)$$

The integral over the whole space to calculate the matrix elements (9.76) can be split into integrations over the unit cells. Thus, the matrix element of the crystal potential in (9.76) can be expressed as

$$(\phi_{\mathbf{G}'}, V(\mathbf{r})\phi_{\mathbf{G}}) = \sum_{s=1}^{N_b} e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}_s} V_s(\mathbf{G}-\mathbf{G}'), \quad (9.79)$$

$$V_s(\mathbf{G}) = \frac{1}{\Omega} \int_{\Omega} V_s(\mathbf{r}) e^{i\mathbf{G}\cdot\mathbf{r}} d^3\mathbf{r}, \quad (9.80)$$

where Ω denotes the volume of the unit cell. The right-hand side of (9.79) consists of the *pseudopotential form factors* V_n and the structure factors.

As one approach, the pseudopotential form factors can be considered as given parameters for a given structure. Similarly to the tight-binding method, a small database containing form factors for a series of semiconductors is provided by GTPack. In general, to handle databases for form factors, **GTPwDatabaseInfo**, **GTPwDatabaseRetrieve**, and **GTPwDatabaseUpdate** can be used.

Conversely, the pseudopotential form factors can be calculated by a FOURIER transform of an ionic model potential in real space. The local HEINE–ABARENKOV pseudopotential is defined as a screened ionic potential of the following form

$$V_{\text{ionic}}(r) = \begin{cases} -V_0 = -\frac{Ze^2}{R_m} u & r < R_m \\ -\frac{Ze^2}{r} & r \geq R_m \end{cases}. \quad (9.81)$$

The effective charge Z , the core radius R_m , and the constant potential in the core region are adjustable parameters. The limiting case of the local HEINE–ABARENKOV pseudopotential ($u \rightarrow 0$) is the so-called empty-core pseudopotential. The FOURIER transform of $V_{\text{ionic}}(r)$ can be computed analytically and is given by

$$V_{\text{ionic}}(q) = -\frac{4\pi Ze^2}{\Omega q^2} \left\{ (1-u) \cos(qR_m) + u \frac{\sin(qR_m)}{qR_m} \right\}. \quad (9.82)$$

The pseudopotential itself is found by screening of the ionic model potential

$$V(q) = \frac{V_{\text{ionic}}(q)}{\varepsilon(q)}. \quad (9.83)$$

Here, $\varepsilon(q)$ denotes the dielectric function, derived by LEVINE and LOUIE [139–141, 143].

Example 55 (Band structure of GaAs using the pseudopotential approach). A band structure calculation of GaAs using the pseudopotential method as implemented within GTPack is shown in Figure 9.16. The zinc blende crystal structure is retrieved from the crystal structure database GTPack.struc by using the commands **GTLoadStructures** and **GTGetStructure**. The definition of the pseudopotential is taken from the database PseudoPot.parm using **GTPwDatabaseRetrieve**.

Mathematica

GTPwDatasetRetrieve, GTPwPrintParmSet, GTPwHamiltonian

Load structure database, select zinc blende structure, adapt to GaAs.

```
In[8]:= GTLoadStructures["GTPack"]; spcGaAs = GTGetStructure["ZnSe", GOverbose -> False] /.
  {"Zn" -> "Ga", "Se" -> "As", 566.8 -> 565.3}
1 structure found in spcgrp.
```

```
-----
Out[8]:= {{ZnSe, Zinc Blend}, cf8, B3, F43m, 208, {{0,  $\frac{a}{2}$ ,  $\frac{a}{2}$ }, { $\frac{a}{2}$ , 0,  $\frac{a}{2}$ }, { $\frac{a}{2}$ ,  $\frac{a}{2}$ , 0}},
  {{(0, 0, 0), Ga}, {{ $\frac{a}{4}$ ,  $\frac{a}{4}$ ,  $\frac{a}{4}$ }, As}}, {a -> 565.3}}
```

Retrieve pseudopotential parameters from database.

```
In[9]:= ppGaAs = GTPwDatabaseRetrieve["PseudoPot", 5]; GTPwPrintParmSet["PseudoPot", 5]
```

Name	GaAs
PP type	PFCoeff
Source	Cohen, Bergstresser
Reference	Phys. Rev. 141, 789 (1966)

reciprocal lattice vectors:

1	2	3	4
$\sqrt{3}$	2	$2\sqrt{2}$	$\sqrt{11}$

Pseudopotential coefficients:

Atom	1	2	3	4
Ga	-0.08	0.025	0.005	0.035
As	-0.15	-0.025	-0.005	0.025

Units : Ryd

Construct the empirical pseudopotential Hamiltonian

```
In[10]:= ham = GTPwHamiltonian[spcGaAs, 5, ppGaAs, GOLattice -> {a -> 1}];
137 lattice vectors
```

Calculate and plot the band structure.

```
In[11]:= kp = GTBZPath["fcc"]; GTBandStructure[ham, kp, 80, 20,
  Joined -> True, PlotLabel -> "", FrameLabel -> {"", "Energy (eV)"},
  PlotRange -> {{0, 4.49}, {-5, 7}}, GOShift -> 8.7, PlotStyle -> Black]
Maximum Abscissa = 4.48735
```

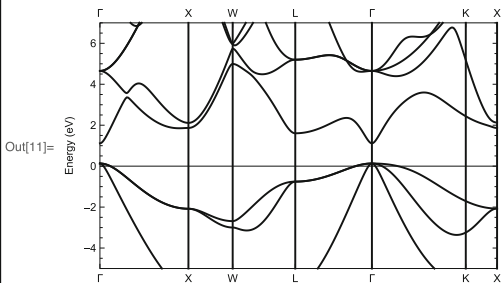


Figure 9.16 Calculation of the band structure of GaAs with form factors from COHEN and BERGSTRESSER [142].

Analogously to [142], pseudopotential form factors to four reciprocal lattice vectors are used and relativistic effects are not taken into account¹⁸⁾. **GTPwHamiltonian** constructs the empirical pseudopotential Hamiltonian. Since the calculation of the bands is done by solving a matrix eigenvalue problem, the same methods as presented for the tight-binding Hamiltonian can be applied. Furthermore, **GTBZPath** is used to obtain a path along high symmetry points within the Brillouin zone of the fcc structure and **GTBandStructure** is used to finally calculate and plot the band structure.

9.6
Electronic Energy Bands and Irreducible Representations

Band structures and symmetry	
GTTbHamiltonianOnsite	Incorporates crystal field splitting of on-site elements
GTTbParmToRule	Substitution rule for TB-parameters
GTTbSymmetryBands	Symmetry analysis of a band structure
GTTbSymmetryPoint	Symmetry analysis of bands at a special k point
GTSymmetrySingleBand	Symmetry analysis of a single band at a given k point
GTBandsPlotImprove	Improve plots with labels of irreducible representations

Corresponding to the fundamental theorems of irreducible representations for symmorphic and nonsymmorphic space groups (cf. Sections 6.4 and 6.5) irreducible representations can be associated with electronic energy bands. Here, the discussion concentrates on symmorphic space groups. Furthermore, gold is taken as an example. The structure of gold is face-centered cubic (symmorphic space group #225). An adequate basis for a tight-binding Hamiltonian consists of *s*-, *p*-, and, *d*-orbitals. The construction of such a Hamiltonian is explained in Figure 9.17. Cu serves as the prototype structure for space group #225. Thus, setting up the Hamiltonian starts from this information in the database **GTPack.struc**. A spherical cluster of atoms is built using **GTCluster**. Using **GTShells**, the cluster is reordered in shells and the list **latt** contains the structural information for the construction of the tight-binding Hamiltonian. **basis** contains the information about the atoms in the unit cell, i.e., one Cu atom with angular momenta 0, 1, 2 (*s*, *p*, and *d*).

The calculation of the band structure and of the density of states of Au is shown in Figure 9.18. First, the Hamiltonian has to be modified slightly. The parameter sets given in [144, 145] take into account the on-site crystal field splitting of the *d*-level. Within the standard construction of the tight-binding Hamiltonian in **GTPack** this effect is not considered. However, by applying **GTTbHamiltonianOnsite** crystal field splitting can be incorporated and the parameter (*dd0*)

18) See Section 9.7.4 for a tight binding calculation for GaAs including spin-orbit coupling.

Mathematica

```

Load fcc structure (Cu is prototype) from database.

In[8]:= GTLoadStructures["GTPack"]; fcc = GTGetStructure["Cu", GOverbose -> False];
1 structure found in spcgrp.

-----

Create a cluster of atoms and reorder the cluster in shells for the Hamiltonian construction.

In[9]:= c1 = GTCluster[fcc, 1.5, GOLattice -> {a -> 1}]; basis = fcc[[7]] /. {a -> 1};
55 atoms
Atoms in cluster: {{Cu, 55}}

In[10]:= latt = GTShells[c1, basis, {2}, GOverbose -> True, GOTbLattice -> {{{"Cu,Cu", {1, 2}}}}];

```

Basis	dist	Atoms	dist	Atoms
Cu	$\frac{1}{\sqrt{2}}$	{{Cu, 12}}	1	{{Cu, 6}}

```

Specify the basis and construct the Hamiltonian.

In[11]:= basis = {{{"Cu", 1, {0, 1, 2}}}}; Hfcc = GTTbHamiltonian[basis, latt];
Store the Hamiltonian for further use (The Hamiltonian does not contain Cu-specific information).

In[12]:= GTWriteToFile[Hfcc, "fcc_spd.ham"]

```

Figure 9.17 Construction of a tight-binding Hamiltonian in two-center approximation for fcc structures with *spd*-basis. Copper represents the prototype structure.

is expressed in terms of two parameters (*dd1*) and (*dd2*). The dataset stored in TB_Handbook.parm contains both, the parameters (*dd1*) and (*dd2*) taking into account the crystal field splitting as well as a parameter (*dd0*) given by the mean value of (*dd1*) and (*dd2*). GTTbParmToRule expresses the symbolic tight-binding parameters of the Hamiltonian by the parameters for a special system from a database in terms of a *Mathematica* substitution rule. Finally, HAup is the TB-Hamiltonian for Au to be used for further calculations. The density of states is calculated first, to determine the FERMI energy.

For the example of gold, the point group of the lattice $\mathcal{G}_0$ is given by O_h . Since a symmorphic space group is considered, the BLOCH function of each energy state transforms as an irreducible representation Γ^p of the group of the wave vector $\mathcal{G}_0(\mathbf{k})$. The wave function $\phi_{\mathbf{k},v}(\mathbf{r})$ is a linear combination of BLOCH functions constructed from atomic orbitals (see equation (9.29)). In Section 9.3.2 it was shown that a BLOCH function constructed from an atomic orbital has the same symmetry properties as the orbital itself. The atomic orbital consists of a spherically symmetric radial part and an angular part. The latter determines the rotational symmetry. Cartesian tesseral harmonics (see Appendix A.2.2) are used within the tight-binding method. Thus, the symmetry properties of $\phi_{\mathbf{k},v}(\mathbf{r})$ in the case of the band structure of Au are found by analyzing

$$\tilde{\phi}_{\mathbf{k},v}(\mathbf{r}) = \sum_{l=0}^2 \sum_{m=-l}^{+l} c_{lm}^v(\mathbf{k}) S_l^m(x, y, z). \quad (9.84)$$

The coefficients $\mathbf{c}^v(\mathbf{k}) = \{c_{lm}^v(\mathbf{k})\}$ are the eigenvectors of the tight-binding Hamiltonian with band index v at $\mathbf{k}$.

Mathematica

Read Hamiltonian from file.

```
In[8]:= Hfcc = GTReadFromFile["fcc_spd.ham"];
```

Correct the diagonal elements for crystal - field splitting and parametrize Hamiltonian.

```
In[9]:= Hfcc1 = GTTbHamiltonianOnsite[Hfcc, {{ "Au", 1, {0, 1, 2} }}, "fcc"];
Aup = GTTbDatabaseRetrieve["TB_Handbook", "Au"];
HAup = Hfcc1 /. GTTbParmToRule[Aup];
```

Calculate density of states and band structure.

```
In[12]:= dosp = {6, 1, -.3, .7, 501, 0.0075, 1};
kdos = GTTDensityOfStates[HAup, "fcc", dosp, GPlotDos -> "ALL",
  PlotStyle -> {Black, {Dotted, Black}}, PlotLabel -> "DOS of Au",
  FrameLabel -> {"Energy (Ryd)", "DOS (states/Ryd)", " ", "IDOS (states)"},
  GOFermiEnergy -> 5.5];
```

```
nkp = 1505
```

```
1505 k-points calculated
```

```
integrated DOS = 5.79467
```

```
Fermi Energy  $E_F$  = 0.524457 (units see band structure)
```

```
In[14]:= kp = GTBZPath["fcc"]; bands = GTBandStructure[HAup, kp, 30, 9, Joined -> True,
  PlotLabel -> "Band structure of Au", FrameLabel -> {" ", "Energy (Ryd)"},
  PlotStyle -> Black,
  GOFermiEnergy -> 0.5245, PlotRange -> {{0, 4.493}, {-0.3, 0.75}}];
Maximum Abscissa = 4.48735
```

```
In[15]:= GraphicsRow[{bands kdos}]
```

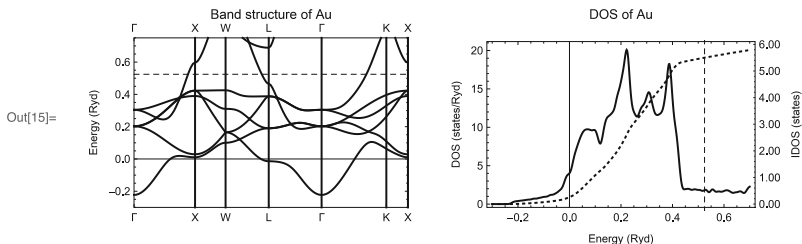


Figure 9.18 Calculation of band structure and density of states of Au without spin-orbit coupling.

The symmetry analysis based on (9.84) can be done by applying the character projection operator. The method is implemented in **GTTbSymmetryBands** and an example is shown in Figure 9.19. Information about the structure and the point group (O_h in the present case) together with a band structure calculation along the symmetry lines are the input data for the symmetry analysis. The definition of the path in the BRILLOUIN zone fixes the points for symmetry analysis. Within this example, only the high symmetry points are analyzed. Internally, **GTTbSymmetryBands** calls **GTTbSymmetryPoint** performing the analysis at a single **k**-point in the BRILLOUIN zone. The module is based on **GTTbSymmetrySingleBand**, analyzing a single band at a single **k**-point. The results of the analysis are provided in tabular form or as a band structure plot as in Figure 9.19. The names of irreducible representations are attached automatically to the bands in the plot. In case the la-

Mathematica

Structural information and installation of point group.

```
In[8]:= bas = {{1, 1, 0}, {0, 1, 1}, {1, 0, 1}};
rbasis = GTReciprocalBasis[bas]/ $\pi$ ;
ohs = GTInstallGroup[Oh, GVerbose  $\rightarrow$  False];
```

Calculation of band structure for symmetry analysis.

```
In[10]:= kp = GTBZPath["fcc"];
kps = GTBZLines[kp, {50, 50, 50, 50, 50, 50}];
klist = kps[[2]]
eigen =
  GTBands[HUp, kps, 9, GOEigenvectors  $\rightarrow$  True, GOSTore  $\rightarrow$  {"Au.bnd", "Au.wav"}];
```

```
Out[10]:= {{1,  $\Gamma$ }, {50, X}, {99, W}, {148, L}, {197,  $\Gamma$ }, {246, K}, {295, X}}
```

Write to file: Au.bnd

Write to file: Au.wav

Perform symmetry analysis.

```
In[12]:= basis = {"Au", 1, {0, 1, 2}};

In[14]:= symma = GTTBSymmetryBands["Au.bnd", klist, "Au.wav", 1, 9,
  ohs, rbasis, basis, PlotLabel  $\rightarrow$  "Band structure of Au",
  FrameLabel  $\rightarrow$  {"", "Energy (Ryd)", PlotRange  $\rightarrow$  {{0, 4.65}, {-0.3, 0.75}},
  GOIrepNotation  $\rightarrow$  "Bouckaert", GOPlot  $\rightarrow$  True, GVerbose  $\rightarrow$  False,
  GOLabelShift  $\rightarrow$  {0.05, 0}, GOLabelStyle  $\rightarrow$  {Black, 13}, PlotStyle  $\rightarrow$  Black]
```

Points	1	2	3	4	5	6	7	8	9
Γ	1	25'	25'	25'	12	12	15	15	15
	-0.2228	0.2024	0.2024	0.2024	0.3045	0.3045	1.8952	1.8952	1.8952
X	1	3	2	5	5	4'	1	5'	5'
	0.0104	0.0291	0.3898	0.4231	0.4231	0.5975	0.8887	1.3779	1.3779
W	2'	3	3	1	1'	1	3	3	2
	0.1004	0.1652	0.1652	0.3103	0.4254	0.8425	1.0799	1.0799	1.2688
L	1	3	3	3	3	2'	1	3'	3'
	-0.0141	0.1901	0.1901	0.388	0.388	0.4654	0.689	1.636	1.636
Γ	1	25'	25'	25'	12	12	15	15	15
	-0.2228	0.2024	0.2024	0.2024	0.3045	0.3045	1.8952	1.8952	1.8952
K	1	1	4	3	2	1	4	1	3
	0.0633	0.1091	0.2625	0.33	0.3963	0.814	0.9336	1.1164	1.4375
X	1	3	2	5	5	4'	1	5'	5'
	0.0104	0.0291	0.3898	0.4231	0.4231	0.5975	0.8887	1.3779	1.3779

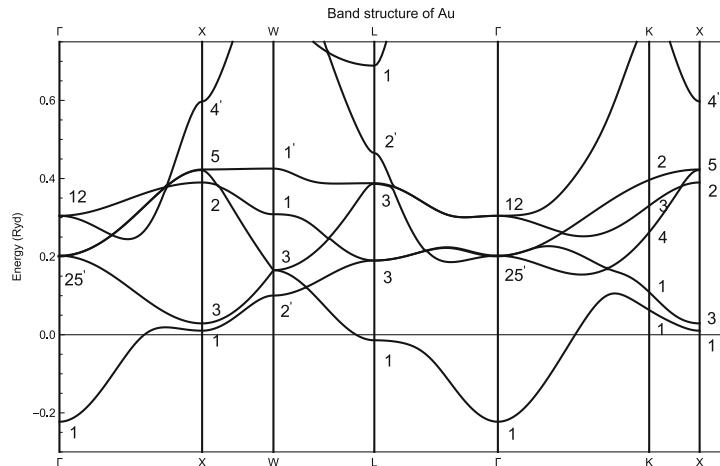


Figure 9.19 Symmetry analysis of the band structure of Au.

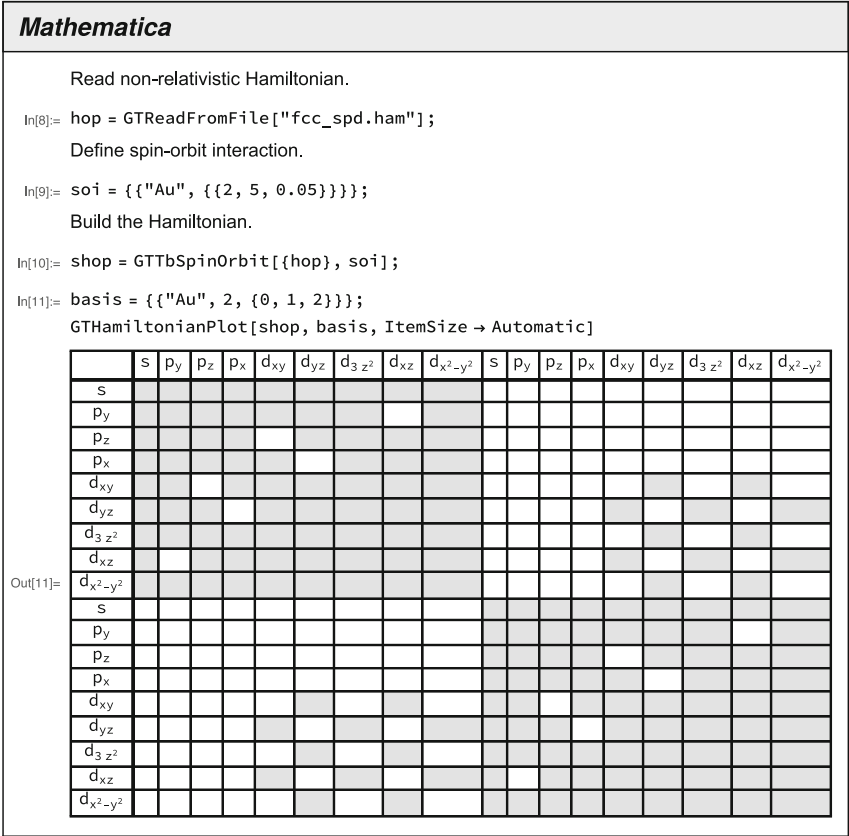


Figure 9.20 Tight-binding Hamiltonian of Au including spin–orbit interaction.

bels have to be shifted or changed the command **GTBandsPlotImprove** and/or the interactive drawing tools of *Mathematica* can be applied¹⁹⁾.

For a realistic result, relativistic effects cannot be neglected when calculating the band structure of Au. As explained in Section 9.4.3, spin–orbit coupling (SOC) can be included easily. Including SOC doubles the size of the Hamiltonian from 9×9 to 18×18 (see Figure 9.20). The eigenvalue problem is expressed in terms of spinors. Within the 18-dimensional eigenvector, the first nine components $\mathbf{c}^v(\mathbf{k})$ correspond to spin-up components, whereas the second nine correspond to spin-down components. Hence, (9.84) can be written as

$$\tilde{\varphi}_{\mathbf{k},v}(\mathbf{r}) = \sum_{l=0}^2 \sum_{m=-l}^{+l} c_{lm}^{v\uparrow}(\mathbf{k}) S_l^m(x, y, z) \chi^\uparrow + \sum_{l=0}^2 \sum_{m=-l}^{+l} c_{lm}^{v\downarrow}(\mathbf{k}) S_l^m(x, y, z) \chi^\downarrow. \quad (9.85)$$

The symmetry analysis is based on the extra representations of the double groups. Automatic generation of double groups and extraction of the extra repre-

19) The automatic generation of the names of irreducible representations can fail if bands are close to each other, because the labels will overlap. See also Section 12.2 for an example.

Mathematica

Implementation of O_h^D and of the standard names of extra representations.

```
In[8]:= ohd = GTInstallGroup["Oh", GOREpresentation -> "SU(2)xS"]; replist =
  {{ "Γ6", "Γ6", "Γ7", "Γ7", "Γ8", "Γ8" },
  { "X6", "X7", "X6", "X7" }, { "W6", "W7" },
  { "L5", "L4", "L4", "L5", "L6", "L6" },
  { "Γ6", "Γ6", "Γ7", "Γ7", "Γ8", "Γ8" },
  { "K5" }, { "X6", "X7", "X6", "X7" }};

The standard representation has changed to SU(2)xS

Reciprocal basis vectors for fcc lattice.

In[9]:= bas = {{1, 1, 0}, {0, 1, 1}, {1, 0, 1}}; kbasis = GTReciprocalBasis[bas] / π;
  ■ information about the orbitals in the basis

In[10]:= basis = {{ "Au", 2, {0, 1, 2} }};

In[11]:= GTTbSymmetryBands["Au_so.bnd", klist, "Au_so.wav", 1, 18, ohd, kbasis,
  basis, PlotLabel -> "Band structure of Au with SO coupling",
  FrameLabel -> { " ", "Energy (Ryd)" },
  PlotRange -> {{0, 4.65}, {-0.25, 1.0}}, GOIrepNotation -> replist,
  GOPlot -> True, GOSpinOrbit -> True, GOLabelStyle -> {Black, 13}, PlotStyle -> Black]
```

Figure 9.21 Symmetry analysis for the relativistic band structure of Au.

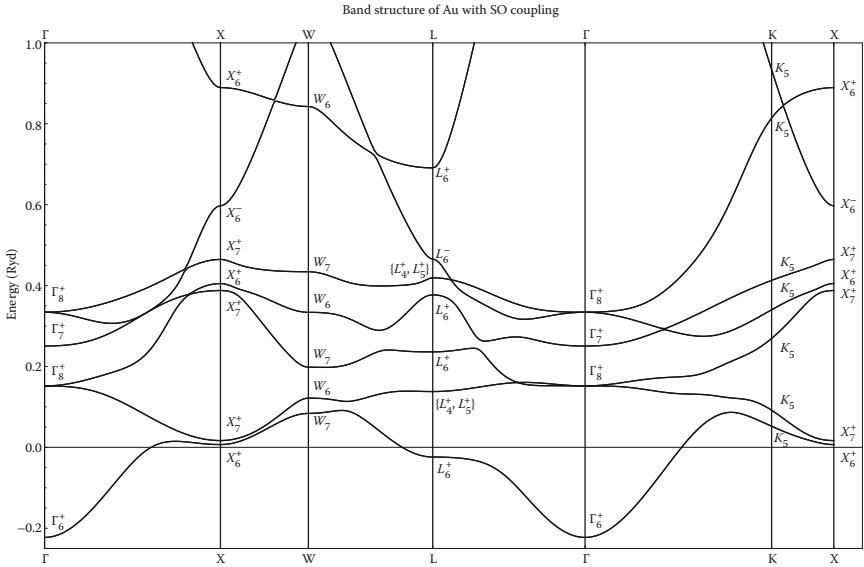


Figure 9.22 Relativistic band structure of Au.

representations is implemented in GTPack and can therefore be used for the symmetry analysis. At the current state, the irreducible representations of double groups are indexed by integers. However, if the double group character tables of the groups $G_0^D(\mathbf{k})$ at the symmetry points are investigated beforehand, a list of names for the extra representations can be provided to **GTTbSymmetryBands**.

Figure 9.21 demonstrates the symmetry analysis of the relativistic Au band structure. The results are shown in Figure 9.22. They are in perfect agreement with *ab initio* band structure calculations [146–148].

9.7
Examples and Applications

FERMI surfaces and other applications	
GT FermiSurface	Calculates the FERMI surface
GT FermiSurfaceCut	Cut through the FERMI surface
GT FermiSurfaceXSF	Exports FERMI surface data to XCrySDen format
GTTbTubeBands	Calculates the band structure of carbon nanotubes
GTAdjacencyMatrix	Calculates the adjacency matrix
GTTbHamiltonianRS	Constructs a real-space Hamiltonian
GTTbRealSpaceMatrix	Gives an interaction matrix between atoms in real space
GT DensityOfStatesRS	Calculates the density of states for a real-space Hamiltonian
GT FindStateNumbers	Finds state numbers within a specified energy region of the spectrum of a real-space Hamiltonian
GT PlotStateWeights	Plots weights of atoms within an eigenstate of a real-space Hamiltonian

9.7.1
Calculation of FERMI Surfaces

The FERMI surface of a material can be calculated from the tight-binding Hamiltonian. The FERMI energy E_F itself is obtained from a density of states calculation, by solving the equation

$$N \stackrel{!}{=} \int_{-\infty}^{E_F} n(E) dE , \tag{9.86}$$

where the total number of electrons N is fixed. To obtain the FERMI surface it is necessary to figure out which bands are cut by the FERMI energy. If several bands are involved, the FERMI surface consists of multiple parts and has a complicated topology.

Figure 9.23 shows the FERMI surface of Cu, calculated using the GTPack command **GT FermiSurface**. The corresponding band structure is calculated with an orthogonal basis and a two-center formulation, using the parameters from [144], given partially in `GT Handbook.parm`. The accuracy of the result, compared with *ab initio* calculations, depends strongly on the quality of the model Hamiltonian. In particular, this is important if small pockets belong to the FERMI surface. However, in the present case of Cu only the 6th band contributes and the FERMI surface has a compact form.

20) For the construction of the BRILLOUIN zone see **GT VoronoiCell**. Within the module, the convex hull algorithm of *Mathematica* is used. Therefore, some artificial lines appear at the BRILLOUIN zone boundary.

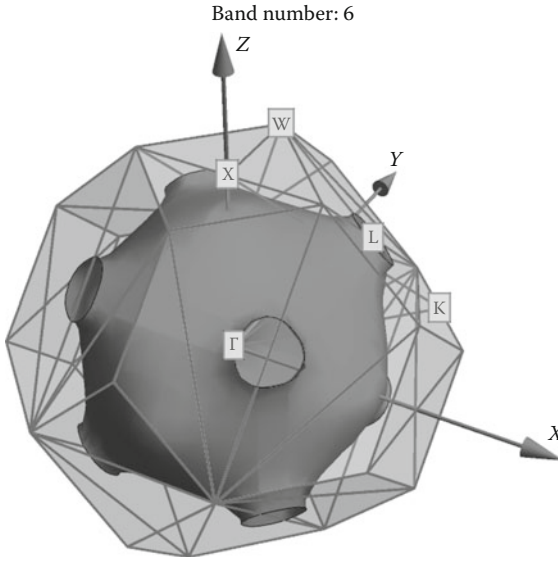


Figure 9.23 FERM surface of Cu ($E_F = 0.5688$ Ry). Additionally, the BRILLOUIN zone and the standard path for band structure calculations are shown.²⁰⁾

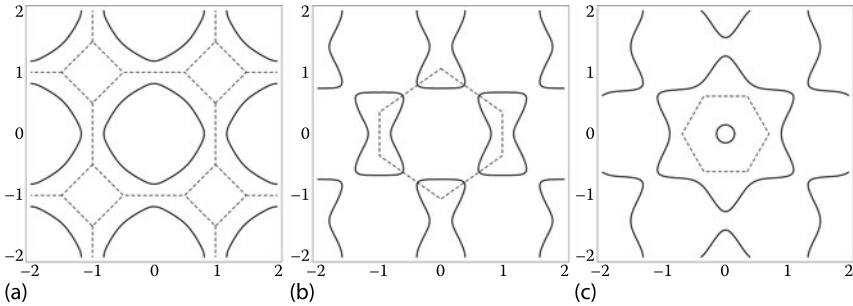


Figure 9.24 Cuts through the FERM surface of Cu (cf. Figure 9.23) The orientation of the cut plane is defined by its normal vector $\mathbf{n}$. The vector $\mathbf{s}$ is a shift of the plane with respect to the Γ point. The vectors $\mathbf{n}$, $\mathbf{s}$ are given in units $2\pi/a$. The BRILLOUIN zone boundary is also indicated (dashed lines). (a) $\mathbf{n} = (0, 0, 1)$, $\mathbf{s} = (0, 0, 0)$; (b) $\mathbf{n} = (1, 1, 0)$, $\mathbf{s} = (0, 0, 0)$; (c) $\mathbf{n} = (1, 1, 1)$, $\mathbf{s} = (.5, .5, .5)$.

A popular program to visualize crystalline structures is XCrySDen [149]. It provides interfaces to *ab initio* electronic structure codes to visualize densities and FERM surfaces. **GTfermiSurfaceXSF** serves as an interface of GTPack to XCrySDen. The command automatically generates the FERM surface data from a given Hamiltonian and exports it to the **bxsf** format, readable by XCrySDen.

Another way to illustrate the topology of the FERM surface is given by considering a cut of the FERM surface with a plane in the BRILLOUIN zone. Three different cuts are presented in Figure 9.24 for Cu, generated using **GTfermiSurfaceCut**. In the free-electron picture the FERM sphere of Cu is inside the first BRILLOUIN

zone. The band energy decreases for electrons in the crystal near the BRILLOUIN zone boundary. Thus, the FERMI surface of Cu touches the BZ boundary near the L point and forms the characteristic necks. The FERMI surface has to impinge perpendicularly upon the hexagonal boundary plane of the BZ due to periodicity in $\mathbf{k}$ -space. Figure 9.24a presents the cut in the k_x - k_y plane using the extended zone scheme. The squares are boundary planes around X points of BRILLOUIN zones in a layer below the considered one. Because the FERMI surface does not touch the zone boundary at X the squares are empty. The contour is not spherically symmetric, but baggy in all X-directions, reflecting the fourfold symmetry. The cut in Figure 9.24b demonstrates that the bands are crossing the BZ boundary perpendicularly. The typical dog bone structure appears.

Task 33 (Band structure of ferromagnetic Ni). Nickel is a ferromagnetic metal from the $3d$ series with fcc structure. Calculate the band structure and the density of states for the two spin directions. Calculate the FERMI energy. What follows for the magnetic moment? Use a TB-Hamiltonian in two-center form. Take into account nearest and next nearest neighbors. The basis consists of s , p , and d functions. **HINT:** The corresponding Hamiltonian can be found in the directory containing the solutions of all tasks. Otherwise Figure 9.17 contains the details to construct the Hamiltonian. Use the parameters from TB_Handbook.parm

Task 34 (Free-electron FERMI surfaces). Calculate the FERMI surfaces for free-electron systems with fcc and bcc structure. Consider a valence of 1, 2, 3, and 4 (see, for example [150] for comparison).

9.7.2

Electronic Structure of Carbon Nanotubes

The development of the silicon technology that has revolutionized communication and computation over several decades is a tremendous success story. Nevertheless, limitations become more and more obvious and nanocarbons offer a new technology platform. Besides graphene nanoribbons (GNRs) also single-walled carbon nanotubes (SWCNT) offer interesting properties for flexible electronics, sensors, and more [151, 152]. GTPack can be used to demonstrate basic electronic properties of SWCNTs.

The structure of carbon nanotubes was discussed in Section 4.4.1 and Figure 4.19 presents the structure of zigzag and armchair nanotubes generated by means of **GTubeStructure**. Additionally, in Section 9.4.1, Example 54, graphene was discussed in connection to the two-center tight-binding model. The nanotube is constructed by rolling up a graphene sheet. Accordingly, the electronic structure of the nanotube is obtained by zone-folding of the dispersion relation of the graphene sheet.

Mathematica GTTubeBands

Read the parametrized Hamiltonian of Graphene from file.

```
In[8]:= ham = GTReadFromFile["Graphene.ham"];
```

Calculate the bands for the (5,5) armchair nanotube for band structure plot an density of states

```
In[9]:= bands = GTTbTubeBands[ham, 5, 5, {{-.5, .0, 200}}, {"x", "Γ"}];
dos = GTTbTubeBands[ham, 5, 5, {{-.5, 0., 1400}}, {"x", "Γ"}],
GOPlotBands → False, GOVerbose → False];
```

20 bands at 200 k-points

Use standard commands to calculate the band structure and density of states.

```
In[11]:= gbands = GTBandsPlot[bands, 20, Joined → True,
PlotRange → {{0, .51}, {-3, 3}}, PlotLabel → "",
FrameLabel → {" ", "Energy / |(ppπ)1|"}, PlotStyle → Black];
Maximum Abscissa = 0.5
```

```
In[12]:= parm = {-3.5, 3.5, 701, .001, 1};
gdos = GTDensityOfStatesPlot[dos, parm,
FrameLabel → {"Energy / |(ppπ)1|", "DOS (arb. units)"}, PlotLabel → "",
PlotStyle → {Black, Black}, PlotRange → {{-4, 4}, {0, 25}}];
```

```
In[14]:= Grid[{{gbands, gdos}}]
```

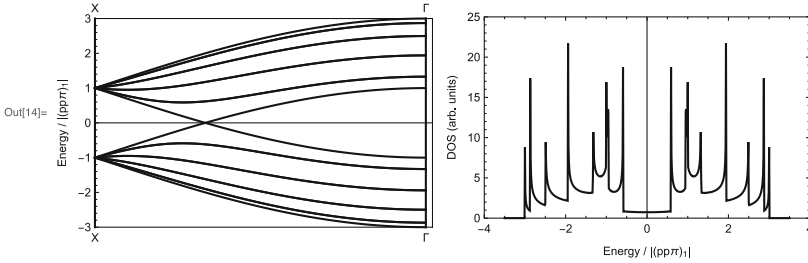


Figure 9.25 Calculation of band structure and density of states for a (5,5) armchair carbon nanotube (π -band approximation, $p_0^{C1} = p_0^{C2} = 0$, $(pp\pi)_1^{C1,C2} = -1$).

If the energy relation of the graphene sheet $E_{g2D}(\mathbf{k})$ is known, the one-dimensional dispersion relation for the nanotube is obtained by

$$E_\mu = E_{g2D} \left(k \frac{\mathbf{K}_2}{|\mathbf{K}_2|} + \mu \mathbf{K}_1 \right), \quad \mu = 0, \dots, N-1, \quad -\frac{\pi}{T} < k < \frac{\pi}{T}. \quad (9.87)$$

The vector $\mathbf{K}_2$ is a reciprocal lattice vector pointing along the nanotube axis and $\mathbf{K}_1$ a vector in the circumferential direction. In the π -band approximation N pairs of bonding π and antibonding π^* bands will be the result of the zone folding process. Here, N denotes the number of hexagons per unit cell (cf. **GTTubeParameters**, see [66]). Consequently, the full Hamiltonian leads to even more bands. The size of the one-dimensional BRILLOUIN zone is defined by the length of the translation vector $T = |\mathbf{T}|$.

GTTubeBands performs the zone folding in such a way that the usual **GTPack** commands can be applied. Figure 9.25 reveals the calculation for the (5,5) arm-

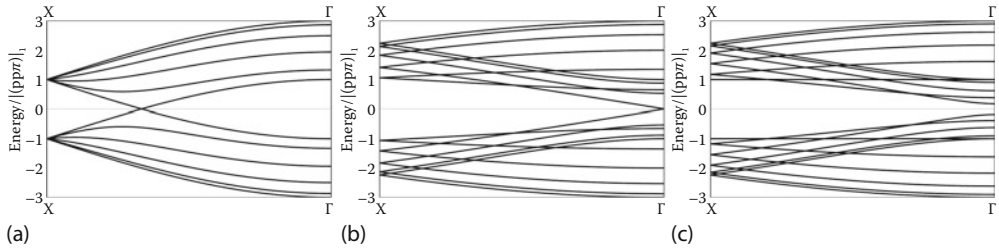


Figure 9.26 Band structures for armchair and zigzag carbon nanotubes. (a) (5,5) Armchair; (b) (9,0) zigzag; (c) (10,0) zigzag.

chair nanotube. The differences in the band structure of armchair and zigzag nanotubes and the dependence on the tube parameters n, m can be seen in Figure 9.26. Armchair nanotubes show a large degeneracy at the zone boundary $k = \pm\pi/a$ (X point). A linear band crossing occurs at $2/3 \overline{\Gamma X}$ at the Fermi energy. Thus, the (5,5) armchair nanotube is a 1-dimensional Dirac semimetal. This behavior is also reflected within the linear density of states. In general, close to the Dirac crossing the density of states goes as $n(E) \sim E^{d-1}$ [24], where d denotes the dimension of the system ($d = 1$ in the present case). The (9,0) zigzag nanotube (cf. Figure 9.26b) does not show a gap either, having a Dirac crossing at the Γ point. For the (10,0) nanotube a gap is obtained (cf. Figure 9.26c). Dispersionless bands appear at $E = \pm(p p \pi)_1^{C1, C2}$ in the spectrum of the (10,0) nanotube. A more detailed discussion of the electronic structure of armchair and zigzag nanotubes, but also of chiral nanotubes can be found in the book of SAITO *et al.* [66].

9.7.3

Tight-binding Real-Space Calculations

So far, the tight-binding approximation was discussed for periodic systems. These systems can be treated effectively using a $\mathbf{k}$ -space formalism. However, a calculation in $\mathbf{k}$ -space is not possible anymore, if translational symmetry is broken and a real-space formalism has to be considered.²¹⁾ The real-space tight-binding approach is a large eigenvalue problem resulting from the consideration of interactions in a cluster of atoms. Of course, this cluster could be part of a periodic system. However, finite size effects occur. Quasicrystals are systems with long-range order, but without translational symmetry. Parts of GTPack together with appropriate real-space Hamiltonians can be used to study simple models for such systems.

In the following, the semiconductor GaAs is used as an example to discuss the real-space method in comparison to the $\mathbf{k}$ -space formulation. Figure 9.27 illustrates the construction of the $\mathbf{k}$ -space Hamiltonian. A cluster of atoms is built from structural information of the zinc blende structure. **GTSHELLS** collects the

²¹⁾ Sophisticated real-space methods like the recursion method [77, 153–155] are not discussed here.

Mathematica

Load the structure database and select the zinc blende structure. Change the data to GaAs:

```
In[8]:= GTLoadStructures["GTPack"]; spcGaAs = GTGetStructure["ZnSe",
  GOverbose -> False];
spcGaAs[[7, 1, 2]] = "Ga";
spcGaAs[[7, 2, 2]] = "As";
spcGaAs[[8]] = {a -> 563.3};

1 structure found in spcgrp.
```

Prepare the information for the construction of the Hamiltonian:

```
In[10]:= clk = GTCluster[spcGaAs, 1, GOLattice -> {a -> 1}];
bask = spcGaAs[[7]] /. {a -> 1};
shells = {1, 1};
shk = GTShells[clk, bask, shells,
  GOverbose -> True, GOPosition -> "Relative", GOTbLattice -> {{{"Ga,As", {1}},
    {"Ga,Ga", {0}}, {"As,As", {0}}}}];

35 atoms

Atoms in cluster: {{As, 16}, {Ga, 19}}
```

Basis	dist	Atoms
Ga	$\frac{\sqrt{3}}{4}$	{{As, 4}}
As	$\frac{\sqrt{3}}{4}$	{{Ga, 4}}

Construct the Hamiltonian:

```
In[12]:= bas = {{{"Ga", 1, {"s", "p", "s*"}}, {"As", 1, {"s", "p", "s*"}}}};
hGaAs = GTTbHamiltonian[bas, shk];

GaAs parameters into Hamiltonian:
```

```
In[14]:= pGaAs = GTTbDatabaseRetrieve["TB_Semiconductors", 15];
phGaAs = hGaAs /. GTTbParmToRule[pGaAs];
```

Figure 9.27 Construction of a k -space Hamiltonian for the zinc blende structure.

structural information to build the Hamiltonian. A nearest neighbor approximation in two-center formulation with sps^* basis is used. A parameter set from VOGL *et al.* [156] is retrieved from the database. The constructed Hamiltonian is parametrized by means of **GTtParmToRule**. Thus, a 10×10 k -space Hamiltonian $\underline{H} = \underline{H}(\mathbf{k})$ results, which is used to calculate the band structure and density of states (cf. Figure 9.28).

The starting point for the real-space formulation is a cluster of atoms. In parallel to (9.29) the ansatz for the wave function reads²²⁾

$$\phi_\nu(\mathbf{r}) = \sum_{s=1}^{N_s} \sum_{n=1}^{N_b^s} \sum_{\mathbf{t}+\mathbf{r}_s < t_c} c_{\nu}^{n,s}(\mathbf{t} + \mathbf{r}_s) \varphi_n^s(\mathbf{r} - \mathbf{t} - \mathbf{r}_s). \quad (9.88)$$

The index ν denotes the energy levels in the cluster. The vectors $\mathbf{t}$ are lattice vectors of the zinc blende structure and the $\mathbf{r}_s$ represent the positions of Ga and As atoms ($N_s = 2$) relative to the lattice. All atoms located within a sphere of radius

22) The formulation of a more general case, not related to a periodic lattice, is straightforward. In such a case the distance dependence of the parameters has to be taken into account.

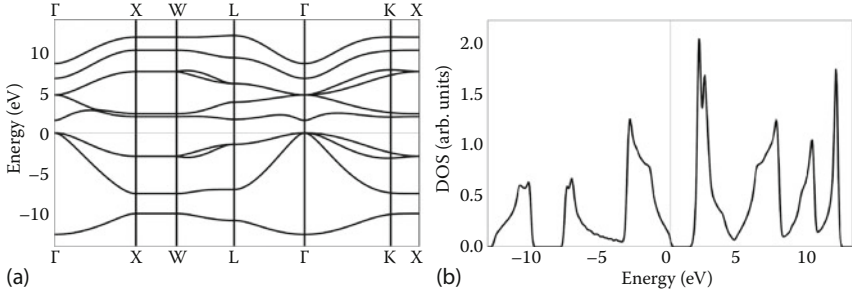


Figure 9.28 Band structure and density of states for GaAs, calculated by means of the tight-binding model according to VOGL *et al.* [156]. (a) Band structure of GaAs. (b) Density of states of GaAs (916 k points in the irreducible part of the BRILLOUIN zone).

Mathematica

GTTbRealSpaceMatrix

```
In[8]:= atom1 = {"A", {"p"}}; atom2 = {"B", {"p"}};
GTTbRealSpaceMatrix[atom1, atom2, 1, G0TbBasis -> 1] // MatrixForm

Out[8]:= MatrixForm[
  (
    (ppπ)1A,B + DM2 (-(ppπ)1A,B + (ppσ)1A,B)      DM DN (-(ppπ)1A,B + (ppσ)1A,B)      DL DM (-(ppπ)1A,B + (ppσ)1A,B)
    DM DN (-(ppπ)1A,B + (ppσ)1A,B)      (ppπ)1A,B + DN2 (-(ppπ)1A,B + (ppσ)1A,B)      DL DN (-(ppπ)1A,B + (ppσ)1A,B)
    DL DM (-(ppπ)1A,B + (ppσ)1A,B)      DL DN (-(ppπ)1A,B + (ppσ)1A,B)      (DN2 + DN2) (-(ppπ)1A,B + (ppσ)1A,B) + (ppσ)1A,B
  )
```

Figure 9.29 Nearest neighbor interaction of p -electrons of atoms A and B. DM, DN, and DL are the direction cosines.

t_c are considered. The size of the real-space Hamiltonian is given by the number of atoms N_{at}^s of sort s in the cluster and the corresponding size of the basis N_b^s ,

$$N_{\text{dim}} = \sum_{s=1}^{N_s} N_{at}^s N_b^s. \quad (9.89)$$

GTTbRealSpaceMatrix is used to construct blocks of the total real-space Hamiltonian. The blocks determine the interaction of two atoms with distance vector $\mathbf{t}_{12}$, depending on the basis sets on both sites. The result is a rectangular matrix expressed in direction cosines of $\mathbf{t}_{12}$ and tight-binding parameters. In Figure 9.29, atoms A and B in nearest neighbor distance are considered and the basis sets consist of p -orbitals only. The interaction is described by a 3×3 matrix. The names of the parameters are constructed automatically. Because of the basis sets, only $(pp\sigma)_1^{A,B}$ and $(pp\pi)_1^{A,B}$ appear.

Figure 9.30 illustrates the construction of the real-space tight-binding Hamiltonian. First, a cluster is constructed that contains the same number of Ga and As atoms. Finally, the cluster consists of 74 atoms. Only nearest neighbor interactions of Ga and As atoms are taken into account. The construction of the Hamiltonian is based on the information stored in the so-called adjacency matrix $\underline{A}$, calculated by **GTAdjacencyMatrix**. The element $A_{i,j}$, $i \neq j$ is zero, if an interaction between the sites i and j does not appear in the Hamiltonian, otherwise it contains information about the interacting atoms.

Mathematica

GTAdjacencyMatrix

Construct the cluster.

```
In[8]:= cl = GTCluster[spcGaAs, 1.3, GOLattice -> {a -> 1}, GOPosition -> {1/8, 1/8, 1/8}];
74 atoms
Atoms in cluster: {{As, 37}, {Ga, 37}}
```

Define the interactions that should be considered in the adjacency matrix.

```
In[9]:= nbto = {{0, (1/4) Sqrt[3]}, {(1/4) Sqrt[3], 0}}; atbto = {"Ga", "As"};
nmat = {nbto, atbto};
GTNeighborPlot[nmat]
```

Out[10]=

	Ga	As
Ga	0	$\frac{\sqrt{3}}{4}$
As	$\frac{\sqrt{3}}{4}$	0

Find the adjacency matrix.

```
In[11]:= admat = GTAdjacencyMatrix[cl, nmat]; GTAdjacencyMatrix[cl, nmat, GOPlot -> True]
```

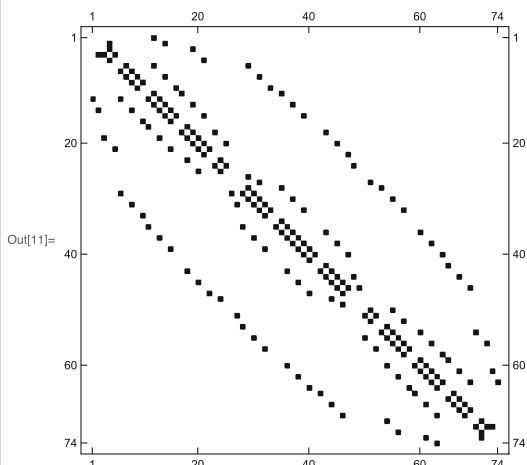


Figure 9.30 Construction of a real-space tight-binding Hamiltonian for GaAs.

The matrices $\underline{A}$ and $\underline{H}$ are sparse matrices. For example, an fcc structure with one s -orbital per site is considered and 1000 atoms form the cluster. If only nearest neighbor interactions are allowed, then in each row of the Hamiltonian at most 13 elements are nonzero (note that at the surface of the cluster the number of neighbors is decreased). This refers to 1.3% of all matrix elements. Hence, sparse matrix techniques can be applied to solve related eigenvalue problems.

The Hamiltonian found by means of **GTTbHamiltonianRS** is parametrized in the usual way. To calculate the density of states, the GTPack command **GTDensityOfStatesRS** is used. Figure 9.31 plots the density of states for calculations with different cluster sizes.

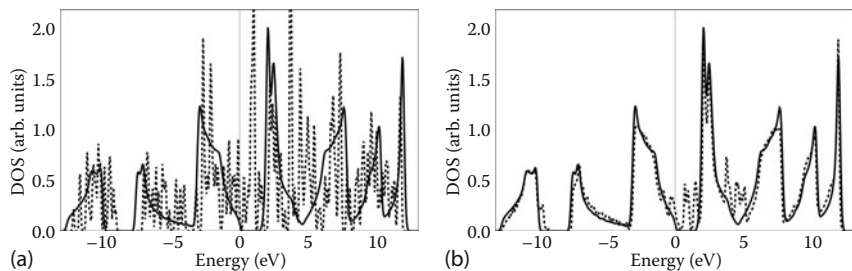


Figure 9.31 Density of states of a real-space tight-binding calculation of GaAs (dashed line) in comparison with the corresponding $\mathbf{k}$ -space calculation (solid line). (a) Comparison of DOS (real-space cluster of 74 atoms); (b) comparison of DOS (real-space cluster of 2146 atoms).

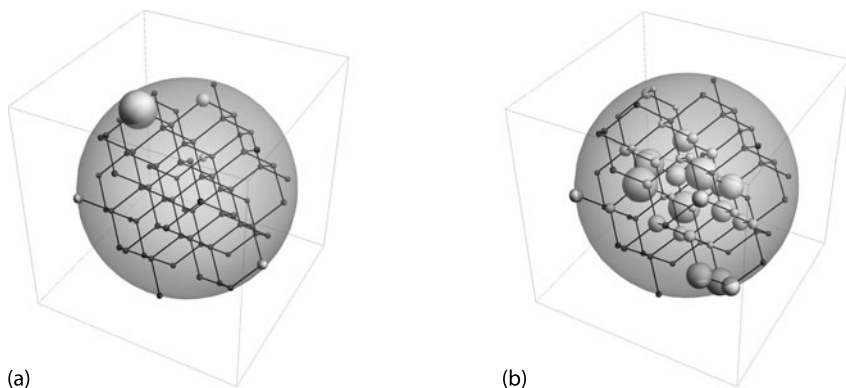


Figure 9.32 Weights of eigenstates for a real-space tight-binding calculation of GaAs at cluster sites of a 74 atom cluster. (a) State 334 ($E_{334} = 1.0026$ eV); (b) state 302 ($E_{302} = -1.9984$ eV).

As can be seen, a cluster of 74 atoms is much too small to lead to a density of states comparable with the $\mathbf{k}$ -space calculation. One reason is that roughly 50% of the atoms of this cluster are located at the surface and the deviation from the $\mathbf{k}$ -space calculation results mainly from surface effects. **GTFindStateNumbers** finds the state numbers in a certain energy window and **GTPlotStateWeights** plots the weights of the state at the cluster sites. The weights are depicted by the size of the spheres at the atomic positions.

The state 334 (cf. Figure 9.32a) in the 74-atom cluster is a state in the gap region of bulk GaAs. As can be seen, this eigenstate refers to a surface state of the cluster, since the weights of the eigenstate are found exclusively on the surface. State 302 has an energy in the valence band region. The weights are spread over atoms inside the cluster (cf. Figure 9.32b). The increase of the cluster size improves the agreement with the $\mathbf{k}$ -space calculation, but the surface states remain (cf. Figure 9.31b).

Task 35 (Surface-projected band structure). To discuss the appearance of surface states in dependence on relaxations or reconstructions of a surface it is helpful to calculate the so-called surface-projected band structure. Thus, the whole bulk

band structure, dependent on $\mathbf{k} = \mathbf{k}_{\parallel} + \mathbf{k}_{\perp}$ (components of $\mathbf{k}$ parallel and perpendicular to the surface) is projected into the surface Brillouin zone. Project the GaAs band structure (without spin–orbit coupling) to the (100) surface. Use a $\mathbf{k}$ -space TB-Hamiltonian with a $sp^3d^5s^*$ basis. Parameter sets are given in TB_Semiconductors.parm. Compare your results with STRASSER *et al.* [157].

9.7.4

Spin–Orbit Coupling in Semiconductors

According to the band structure in Figure 9.28a, the top of the valence band at Γ is 3-fold degenerate due to the degeneracy of p -orbitals.²³⁾ If spin is included, the degeneracy is 6-fold. It is well known from experiments (optical spectra, spin-polarized photoemission) that the top of the valence band is split into a 4-fold degenerate band and a separate 2-fold band at a small energy below the valence band edge [160]. This effect is caused by spin–orbit coupling and is essential for the function of standard semiconductor devices and a basic effect for modern semiconductor spintronics [161–163].

In the following, the influence of spin–orbit coupling to the energy bands of semiconductors, especially GaAs will be discussed. Previously, in Section 9.7.3 the construction of a $\mathbf{k}$ -space Hamiltonian for the zinc blende structure of GaAs was discussed (see Figure 9.27). In this example, a sp^3s^* Hamiltonian was used to compare the $\mathbf{k}$ -space and the real-space tight-binding model, respectively. Here, the band structure including spin–orbit coupling is calculated by means of a Hamiltonian in a $sp^3d^5s^*$ basis that gives better agreement with more involved *ab initio* calculations. The construction of this Hamiltonian follows the same line as before and will not be repeated in detail (see Task 35). Tight-binding parameters for such a basis are given by JANCU *et al.* [158] for a list of semiconductors and more recently by TAN *et al.* for GaAs [164]. Spin–orbit coupling (SOC) does not influence the s -electrons and therefore needs to be included for the p -electrons only. The band structure of GaAs including spin–orbit coupling is shown in Figure 9.33. The splitting at Γ is shown schematically in Figure 9.33a.

The details of the band structure calculation at Γ are summarized in Figure 9.34. The splitting of states is in accordance with the discussion of Section 8.6.

The standard basis for the construction of the tight-binding Hamiltonian with SOC follows the sequence (p -orbitals only) $p_{y\uparrow}, p_{z\uparrow}, p_{x\uparrow}, p_{y\downarrow}, p_{z\downarrow}, p_{x\downarrow}$. Within this restricted basis a 6×6 Hamiltonian results. However, a rearrangement of the basis using the sequence $p_{y\uparrow}, p_{z\downarrow}, p_{x\uparrow}, p_{y\downarrow}, p_{z\uparrow}, p_{x\downarrow}$ leads to a block diagonal form of this Hamiltonian. This is demonstrated for GaAs at the Γ point using a Hamiltonian with sp basis per atom (cf. Figure 9.35). The transformation of the Hamiltonian can be performed by constructing a permutation matrix using the command **GTReorderMatrix**. The two resulting blocks after the similarity transformation of the Hamiltonian are complex conjugate to each other. Hence, each

23) This can be checked by inspection of the structure of the Hamiltonian at the Γ point by means of **GTHamiltonianPlot** or by inspection of the eigenvectors at Γ .

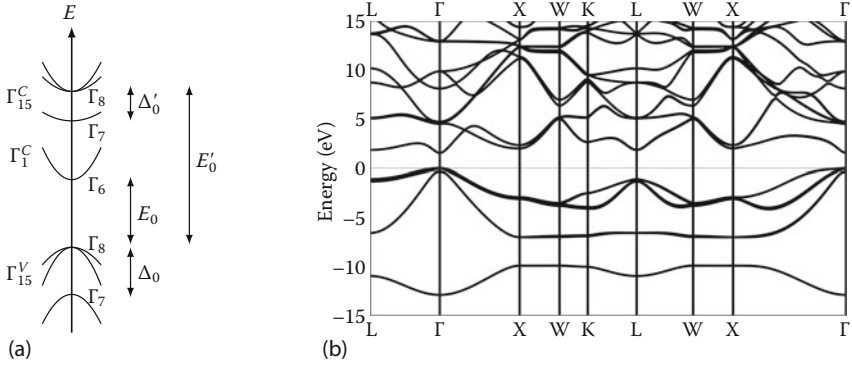


Figure 9.33 Band structure of GaAs with $spds^*$ basis and spin–orbit coupling (parameters taken from [158]) (a) Energy levels at Γ point (adapted from [159]); (b) band structure in the entire BRILLOUIN zone.

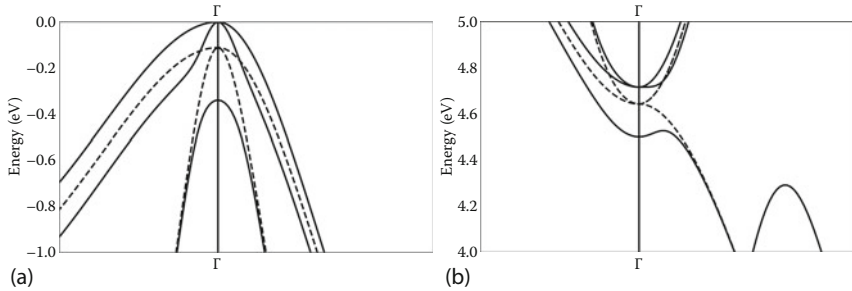


Figure 9.34 Influence of spin–orbit coupling on degenerated eigenstates at the Γ point within the BRILLOUIN zone for GaAs. Because of spin–orbit coupling, the threefold degenerate state belonging to Γ_{15} is split into the twofold degenerated state Γ_8 and Γ_7 . The plot shows the energy dispersion along $L-\Gamma-X$ in the neighborhood of Γ . (a) Splitting of Γ_{15}^V into Γ_7 and Γ_8 ; (b) splitting of Γ_{15}^C into Γ_7 and Γ_8 .

eigenvalue occurs twice. Therefore, it is enough to solve the eigenvalue problem for one block only.

Inspection of the rearranged Hamiltonian shows that the 6×6 eigenvalue problem resulting from p -orbitals consists of two 3×3 on-site blocks (Ga,As) connected by matrix elements representing the nearest neighbor Ga-As interaction. Thus, the splitting at the valence band edge (intraband band contribution Δ_0 in Figure 9.33a) is represented in first order by such a 3×3 block. Without spin–orbit coupling, the block belongs to a three-fold degenerate representation Γ_{15} . The parameter ξ , controlling the spin–orbit coupling, corresponds to $\Delta/3$, i.e., a third of the level splitting $\Delta = E^{\Gamma_8} - E^{\Gamma_7}$. According to Figure 9.33a, the twofold degenerate level belongs to Γ_8 . In general, the level splitting at the Γ point due to spin–orbit coupling can be verified by applying the command **GTSOCSSplitting** as shown in Example 49.

Mathematica

```

In[8]:= cmat = GTReorderMatrix[16, {{3, 11}, {7, 15}}];

In[9]:= hsocr = cmat.hsoc.cmat // Chop;

In[10]:= hplot = GTHamiltonianPlot[hsoc, bas];
hplot1 = GTHamiltonianPlot[hsocr, bas]; Grid[{{hplot, hplot1}}]

```

Out[10]=

```

In[11]:= hmat = {{Ep, 0, 0}, {0, Ep, 0}, {0, 0, Ep}};
smat = {{0, -I, I}, {I, 0, 1}, {-I, 1, 0}}; hop = hmat + ξ smat; hop // MatrixForm

```

Out[11]=MatrixForm=

$$\begin{pmatrix} E_p & -i\xi & i\xi \\ i\xi & E_p & \xi \\ -i\xi & \xi & E_p \end{pmatrix}$$

```

In[12]:= Eigenvalues[hop]

```

Out[12]= {Ep - 2 ξ, Ep + ξ, Ep + ξ}

Figure 9.35 A rearrangement of the basis allows one to work with a Hamiltonian of smaller size (Hamiltonian at Γ point). The eigenvalues of the 3×3 p -matrix reveal the spin-orbit splitting of Γ_{15} .

9.7.5

Tight-Binding Models for Oxides

As a final example for the construction of model Hamiltonians, the class of perovskites, i.e., compounds with the general formula ABO_3 (B – transition metal ion), will be considered. A prototypical crystal structure of the material $SrTiO_3$ is shown in Figure 9.36. This large class of materials shows a variety of interest-

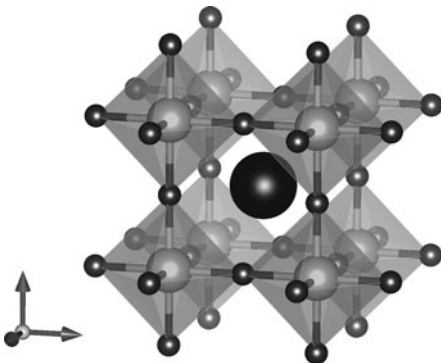


Figure 9.36 Crystal structure of $SrTiO_3$. The light gray atoms represent Ti, the central atom is Sr, and the dark small atoms represent oxygen.

ing properties depending on the specific chemistry of the compounds involved. By breaking the cubic symmetry via moving the central atom in Figure 9.36 out of the center of the structure, perovskites can establish a ferroelectric moment [165]. Typical ferroelectrics well studied within the literature are BaTiO_3 or PbTiO_3 [166, 167]. In the case of SrTiO_3 , a so-called quantum paraelectric behavior is present, where quantum fluctuations at zero temperature between structural ground states suppress the transition to the ferroelectric state [168]. Furthermore, SrTiO_3 is the first discovered oxide superconductor [169]. Additionally, perovskites are discussed in connection to the giant magnetoresistance effect [170] and are therefore considered as candidates for spintronic devices [171]. A comprehensive discussion of electronic and optical properties of perovskites in the framework of tight-binding approximations is given by WOLFRAM and ELLIALTOIĞLU [172].

Within oxide perovskites the transition metal ion is surrounded by an oxygen octahedron as shown in Figure 9.36. The unit cell consists of five atoms. The automatic construction of a two-center tight-binding Hamiltonian in the framework of GTPack is shown in Figure 9.37. The algorithm takes into account that multiple oxygen atoms occur, finally characterized by only one parameter set. This is achieved by indexing the names within the real-space structure (**GTCluster**, **GT-Shells**). Information about this redefinition affects the construction of the Hamiltonian. The special treatment of equivalent atoms guarantees that the parameter set used in the construction of the Hamiltonian are as small as possible.

The first step in constructing a Hamiltonian is the choice of a proper basis and to fix the range of interaction. In most cases of oxide perovskites, the s -states of the A atom do not play a significant role in the electronic structure. Thus, the model concentrates on the BO_3 octahedron and the basis is formed by the d -orbitals of the transition metal together with the oxygen p -orbitals. Only interactions between nearest and second nearest neighbors, i.e., cation-anion and anion-anion (between adjacent oxygen atoms), are considered. The resulting Hamiltonian is represented by a 14×14 matrix and **GTHamiltonianPlot** is used to reveal its structure.

The five atomic functions belonging to the d -states separate into basis functions of the 2-dimensional irreducible representation E_g and the 3-dimensional irreducible representation T_{2g} of the point group O_h . Matrix elements between basis functions at the same site of those irreducible representations have to vanish due to the matrix element theorem (see Section 9.4). A similar argument holds for the oxygen p -orbitals. Thus, all diagonal blocks are determined by the on-site energies only. If crystal field splitting is taken into account, the on-site energies are given by four parameters: E_e for d -electrons with E_g symmetry ($3z^2 - r^2, x^2 - y^2$), E_t describes d -electrons with T_{2g} symmetry (xy, xz, yz), $E_{||}$ is used for p -orbitals parallel to the coordinate axis (e.g., x) orbital at (1,0,0), and finally $E_{\perp}$ stands for p -orbitals perpendicular to the coordinate axis. Finally, Figure 9.38 shows the band structure calculated from the tight-binding Hamiltonian. Because of the simple structure of the Hamiltonian analytic formulas can be easily generated at the high symmetry points of the BRILLOUIN zone. Such formulas are usually used to fit the TB model against *ab initio* band structures (cf.[172]).

Mathematica

Load the Perovskite structure from database.

```
In[8]:= GTLoadStructures["GTPack"]; bto = GTGetStructure["BTO"];
1 structure found in spcgrp.

-----

Prototype      : {BTO, Perovskite}
Pearson Symbol  : cP5
Strukturbericht : E21
Space Group     : Pm $\bar{3}$ m
Number         : 221
Lattice Vectors : {{a, 0, 0}, {0, a, 0}, {0, 0, a}}
Basis Vectors   :
{{(0, 0, 0), Ti}, {{ $\frac{a}{2}$ ,  $\frac{a}{2}$ ,  $\frac{a}{2}$ }, Ba}, {{ $\frac{a}{2}$ , 0, 0}, O}, {{0,  $\frac{a}{2}$ , 0}, O}, {{0, 0,  $\frac{a}{2}$ }, O}}
Lattice Constants : {a → 361.49}

-----
```

Construct the cluster and differentiate between atoms of the same sort.

```
In[9]:= cl = GTCluster[bto, 2, GOLattice -> {a → 1}, GOTbEquivalence -> False];
149 atoms
Atoms in cluster: {{Bal, 32}, {O3, 28}, {Til, 33}, {O2, 28}, {O1, 28}}
```

```
In[10]:= bas = bto[[7]] /. {a → 1}; shells = {3, 3, 3, 3};
```

Collect information for the Hamiltonian construction.

```
In[11]:= sh = GTShells[cl, bas, shells,
  GOverbose -> True, GOTbLattice -> {{{"Ti", Ti}, {0}}, {"O", O}, {0}},
  {"Ti", O}, {1}}, {"O", O}, {2}}, GOPosition -> "Relative"];
GTShells : modified basis :
{{(0, 0, 0), Til}, {{ $\frac{1}{2}$ ,  $\frac{1}{2}$ ,  $\frac{1}{2}$ }, Bal}, {{ $\frac{1}{2}$ , 0, 0}, O1}, {{0,  $\frac{1}{2}$ , 0}, O2}, {{0, 0,  $\frac{1}{2}$ }, O3}}
```

Basis	dist	Atoms	dist	Atoms	dist	Atoms
Til	$\frac{1}{2}$	{{O3, 2}, {O2, 2}, {O1, 2}}	$\frac{\sqrt{3}}{2}$	{{Bal, 8}}	1	{{Til, 6}}
Bal	$\frac{1}{\sqrt{2}}$	{{O1, 4}, {O2, 4}, {O3, 4}}	$\frac{\sqrt{3}}{2}$	{{Til, 8}}	1	{{Bal, 6}}
O1	$\frac{1}{2}$	{{Til, 2}}	$\frac{1}{\sqrt{2}}$	{{Bal, 4}, {O3, 4}, {O2, 4}}	1	{{O1, 6}}
O2	$\frac{1}{2}$	{{Til, 2}}	$\frac{1}{\sqrt{2}}$	{{Bal, 4}, {O3, 4}, {O1, 4}}	1	{{O2, 6}}
O3	$\frac{1}{2}$	{{Til, 2}}	$\frac{1}{\sqrt{2}}$	{{Bal, 4}, {O2, 4}, {O1, 4}}	1	{{O3, 6}}

Construct the Hamiltonian.

```
In[12]:= basis = {{{"Ti", 1, {"d"}}, {"O", 3, {"p"}}}}; Hperov = GTTbHamiltonian[basis, sh];
```

Plot structure of Hamiltonian.

```
In[13]:= GTHamiltonianPlot[Hperov, basis]
```

	d _{xy}	d _{yz}	d _{3 z²}	d _{xz}	d _{x²-y²}	p _y	p _z	p _x	p _y	p _z	p _x	p _y	p _z	p _x
d _{xy}														
d _{yz}														
d _{3 z²}														
d _{xz}														
d _{x²-y²}														
p _y														
p _z														
p _x														
p _y														
p _z														
p _x														
p _y														
p _z														
p _x														

Figure 9.37 Construction of a k-space model Hamiltonian for the perovskite structure.

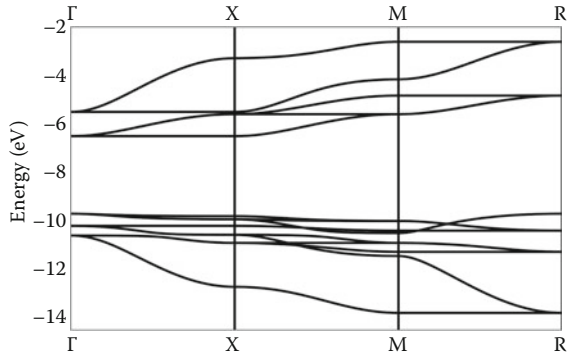


Figure 9.38 Model band structure of the perovskite SrTiO_3 . The following parameters (in eV) are used (see [172], p. 83): $E_e = -5.5$, $E_t = -6.5$, $E_{\parallel} = -10.5$, $E_{\perp} = -10.0$, $(pd\sigma) = -2.0$, $(pd\pi) = 1.0$, $(pp\sigma) = -0.15$, $(pp\pi) = 0.05$.

Part Three

Applications in Photonics

10

Solution of MAXWELL's Equations

Wenn mir EINSTEIN ein Radiotelegramm schickt, er habe nun die Teilchennatur des Lichts endgültig bewiesen, so kommt das Telegramm nur an, weil das Licht eine Welle ist.

Niels Bohr

(from W. RÖSSLER, Eine kleine Nachtphysik, Birkhäuser, 2007)

Starting from MAXWELL's equations, the so-called master equation is derived, which is the basic equation to model photonic crystals (PCs). The equation describes the propagation of electromagnetic waves in periodically structured dielectric materials. In parallel to the group of the SCHRÖDINGER equation, the group of MAXWELL's equations is introduced. Thus, symmetry properties of the photonic crystal determine the symmetry properties of the electromagnetic fields. A numerical scheme for the calculation of photonic band structures, based on a plane-wave expansion is developed. This provides the background for the calculations in the following two chapters.

Previously, the transformation behavior of the SCHRÖDINGER and the PAULI equation was discussed. The resulting group theoretical methods for the investigation and solution of these equations can also be applied to the field of photonics, where the basic equations exhibit a similar structure.

Natural or artificial systems characterized by a periodic modulation of the permittivity are a novel class of optical media, called photonic crystals (PCs). According to the number of directions of periodic permittivity modulations, photonic crystals are classified as one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) PCs, respectively. For example, so-called BRAGG gratings represent 1D-PCs. Si slabs with periodically etched pores, as shown in Figure 1.2b, are 2D-PCs. Consequently, whereas the permittivity is uniform in the nonperiodic directions for 1D and 2D photonic crystals, it is periodic in all three directions for 3D-PCs. Similarly to crystals in the electronic structure theory, this offers a large variety of possible photonic crystal structures. The design of photonic crystals with respect to special applications is a main area of research in the field of photonics.

The complete electronic band gap is a basic property of semiconductors, exploited in solid-state electronics. In the same way a *photonic band gap* can appear in photonic crystals. A complete photonic band gap exists for a certain material, if the propagation of an electromagnetic wave of any polarization of any direction with a frequency in the range of the gap is forbidden.

The application of group theory to properties of photonic crystals follows similar lines as for electronic structure calculations, including a few characteristic differences. The propagation of electromagnetic waves is governed by MAXWELL's equations. Therefore, the symmetry of the PC has to be related to the transformation properties of MAXWELL's equations. In comparison to the wave functions, which are solutions of the SCHRÖDINGER equation, electromagnetic waves are vector fields and follow slightly different transformation properties as discussed in Section 2.2.2. Furthermore, in Section 9.5, it was shown that in many cases the crystal potential can be substituted by a smooth pseudopotential, which is characterized by a few FOURIER components only. This choice leads to a sufficiently small eigenvalue problem for electronic structure calculations. However, in photonic crystals the permittivity is not a smooth function like the crystal potential, leading to convergence problems within the FOURIER expansion. In general, thousands of plane waves are necessary for an exact numerical treatment of photonic crystals. The computational demand of such problems often exceeds the capabilities of *Mathematica* and GTPack. Therefore, more involved calculations will be done by applying the MIT Photonic-Bands package (MPB) [174, 175]. By importing results obtained with MPB, the symmetry properties of the eigenmodes are investigated using GTPack.

10.1

MAXWELL's Equations and the Master Equation for Photonic Crystals

The theoretical description of photonic crystals is discussed in detail in several books [27, 28, 176, 177]. In the following, the basic equations will be discussed with respect to their implementation in GTPack.

10.1.1

The Master Equation

In the following, the propagation of electromagnetic waves in a dielectric medium is considered. Thus, no free charges and no free currents are present and MAXWELL's equations read

$$\nabla \cdot \mathbf{B}(\mathbf{r}, t) = 0, \quad (10.1)$$

$$\nabla \cdot \mathbf{D}(\mathbf{r}, t) = 0, \quad (10.2)$$

$$\nabla \times \mathbf{E}(\mathbf{r}, t) = -\frac{\partial \mathbf{B}(\mathbf{r}, t)}{\partial t}, \quad (10.3)$$

$$\nabla \times \mathbf{H}(\mathbf{r}, t) = \frac{\partial \mathbf{D}(\mathbf{r}, t)}{\partial t}. \quad (10.4)$$

Equations (10.1) and (10.2) describe the sources of the magnetic induction $\mathbf{B}(\mathbf{r}, t)$ and the electric displacement $\mathbf{D}(\mathbf{r}, t)$, respectively. The induction law is reflected in (10.3), i.e., time-dependent magnetic fields cause electric vertices.

Additionally, the *materials equations* (constitutive equations) hold, which, in linear response, relate the magnetic field $\mathbf{H}$ and the magnetic induction $\mathbf{B}$ as well as the electric displacement field $\mathbf{D}$ and the electric field $\mathbf{E}$,

$$\mathbf{B}(\mathbf{r}, t) = \mu_0 \mu_r \mathbf{H}(\mathbf{r}, t), \quad (10.5)$$

$$\mathbf{D}(\mathbf{r}, t) = \varepsilon_0 \varepsilon_r \mathbf{E}(\mathbf{r}, t). \quad (10.6)$$

Here, μ_0 and ε_0 denote the vacuum permeability and permittivity, while μ_r and ε_r denote the relative permeability and permittivity, accounting for a response of matter to a magnetic and electric field, respectively. In the form mentioned above, the relative permeability and permittivity are formulated for an isotropic material. In the case of an anisotropic material they are represented by tensors of rank two.

The magnetic response of dielectric materials at optical frequencies is usually negligible, i.e., $\mu_r = 1$. Within a structure consisting of different dielectric materials, the permittivity will depend on the spatial coordinate, i.e., $\varepsilon_r = \varepsilon_r(\mathbf{r})$. In the case of a photonic crystal this dependence is periodic within a lattice having $\mathbf{t}$ as lattice vectors,

$$\varepsilon(\mathbf{r}) = \varepsilon(\mathbf{r} + \mathbf{t}). \quad (10.7)$$

Making use of equations (10.3) and (10.4) and the constitutive relation (10.6), $\mathbf{B}(\mathbf{r}, t)$ can be eliminated leading to

$$\frac{1}{\varepsilon_r(\mathbf{r})} \nabla \times (\nabla \times \mathbf{E}(\mathbf{r}, t)) = -\frac{1}{c^2} \frac{\partial^2 \mathbf{E}(\mathbf{r}, t)}{\partial t^2}, \quad (10.8)$$

where the vacuum speed of light c is given by

$$c = \frac{1}{\sqrt{\varepsilon_0 \mu_0}}. \quad (10.9)$$

In the same manner, an equation for the magnetic field $\mathbf{H}(\mathbf{r}, t)$ is found

$$\nabla \times \left(\frac{1}{\varepsilon_r(\mathbf{r})} \nabla \times \mathbf{H}(\mathbf{r}, t) \right) = -\frac{1}{c^2} \frac{\partial^2 \mathbf{H}(\mathbf{r}, t)}{\partial t^2}. \quad (10.10)$$

Since the permittivity is time-independent, time and space coordinates are separable in (10.8) and (10.10), leading to a harmonic time dependence of the $\mathbf{E}$ and $\mathbf{H}$ fields. Because of the linearity of the equations, a general time dependence can be decomposed in terms of harmonic contributions by means of a FOURIER analysis. Using a time harmonic ansatz for $\mathbf{E}$ and $\mathbf{H}$ in equations (10.8) and (10.10),

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r}) e^{-i\omega t}, \quad (10.11)$$

$$\mathbf{H}(\mathbf{r}, t) = \mathbf{H}(\mathbf{r}) e^{-i\omega t}, \quad (10.12)$$

finally leads to the so-called *master equations*

$$\frac{1}{\varepsilon_r(\mathbf{r})} \nabla \times (\nabla \times \mathbf{E}(\mathbf{r})) = \frac{\omega^2}{c^2} \mathbf{E}(\mathbf{r}) , \quad (10.13)$$

$$\nabla \times \left(\frac{1}{\varepsilon_r(\mathbf{r})} \nabla \times \mathbf{H}(\mathbf{r}) \right) = \frac{\omega^2}{c^2} \mathbf{H}(\mathbf{r}) . \quad (10.14)$$

These equations are generalized wave equations and express MAXWELL's equations as eigenvalue problems. Since $\mathbf{E}$ and $\mathbf{H}$ are connected by the curl equations (10.3) and (10.4) (having in mind the materials equations (10.5) and (10.6)), only one of the master equations has to be solved. Usually, equation (10.14) is solved, since the operator on the left-hand side is Hermitian. Finally, it has to be noted that any solution of the master equations also has to satisfy the divergence conditions in equations (10.1) and (10.2). Hence, a mathematical solution of the generalized wave equation is not necessarily a solution of MAXWELL's equations.

10.1.2

One- and Two-Dimensional Problems

In the following, the master equations (10.13) and (10.14) are discussed for 1D- and 2D-PCs. In case of 1D-PCs it is assumed that the material is periodic in the x -direction whereas it is isotropic within the yz -plane. The propagation direction of the electromagnetic waves is parallel to the x -axis. Additionally, the polarization direction has to be perpendicular to the propagation direction and, without loss of generality, a polarization in the z -direction can be assumed. For such a photonic crystal the master equations read

$$-\frac{1}{\varepsilon(x)} \frac{\partial^2}{\partial x^2} E_z(x) = \frac{\omega^2}{c^2} E_z(x) , \quad (10.15)$$

$$-\frac{\partial}{\partial x} \frac{1}{\varepsilon(x)} \frac{\partial}{\partial x} H_z(x) = \frac{\omega^2}{c^2} H_z(x) . \quad (10.16)$$

For a 2D-PC it is assumed that the permittivity is periodic in the xy -plane and translational invariant in the z -direction. Furthermore, it is assumed that the light propagates within the xy -plane. Because of the translational invariance in z -direction $\varepsilon(\mathbf{r})$, $\mathbf{E}(\mathbf{r})$ and $\mathbf{H}(\mathbf{r})$ are independent of the z -coordinate. The resulting two linearly independent solutions are given by the so-called transverse magnetic (TM) and transverse electric (TE) modes¹⁾, where the names correspond to the orientation of the field components. In the transverse magnetic (TM) mode the magnetic field components are oriented perpendicular to the z -axis, whereas the electric field components are oriented perpendicular to the z -axis for the transverse electric (TE) mode. Both cases are shown in Figure 10.1.

1) Alternatively, E-polarization and H-polarization can be used for the TM and TE modes.

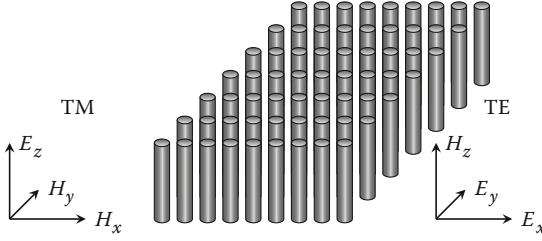


Figure 10.1 Definition of the transverse magnetic (TM) and the transverse electric (TE) modes.

The vectorial MAXWELL's equations are decomposed into two sets of independent equations for the two modes²⁾. The resulting master equations are given by

$$-\frac{1}{\varepsilon(\mathbf{r}_{\parallel})} \left\{ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right\} E_z(\mathbf{r}_{\parallel}) = \frac{\omega^2}{c^2} E_z(\mathbf{r}_{\parallel}), \quad (10.17)$$

$$-\left\{ \frac{\partial}{\partial x} \frac{1}{\varepsilon(\mathbf{r}_{\parallel})} \frac{\partial}{\partial x} + \frac{\partial}{\partial y} \frac{1}{\varepsilon(\mathbf{r}_{\parallel})} \frac{\partial}{\partial y} \right\} H_z(\mathbf{r}_{\parallel}) = \frac{\omega^2}{c^2} H_z(\mathbf{r}_{\parallel}), \quad (10.18)$$

for TM and TE polarization, respectively. Here, the vector $\mathbf{r}_{\parallel}$ denotes a vector in the xy plane.

10.2

Group of the Master Equation

Analogously to the group of the SCHRÖDINGER equation and the group of the PAULI equation (see Section 7.2 and Section 8.4), the group of the master equation can be introduced as the group containing all transformations leaving the master equation invariant. For the sake of brevity, the discussion will be focused on the 2D master equation (10.17) for the TM mode

$$\widehat{M}_E E(\mathbf{r}_{\parallel}) = -\frac{1}{\varepsilon(\mathbf{r}_{\parallel})} \left\{ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right\} E_z(\mathbf{r}_{\parallel}) = \frac{\omega^2}{c^2} E_z(\mathbf{r}_{\parallel}). \quad (10.19)$$

The discussion of the master equation for a TE polarization (10.18) and of the corresponding equations in three dimensions (10.13) and (10.14) follow the same line.

In the following, it will be shown that the two-dimensional space group $\mathcal{R}$ belonging to the symmetry of $\varepsilon(\mathbf{r}_{\parallel})$, i.e.,

$$\widehat{P}(T)\varepsilon(\mathbf{r}_{\parallel}) = \varepsilon(\mathbf{r}_{\parallel}), \quad \forall T = \{\underline{\mathbf{R}}_T \mid \mathbf{t}_{\parallel,T}\} \in \mathcal{R} \quad (10.20)$$

also serves as the group of the master equation. Hence, for all operators $\widehat{P}(T)$ associated with the group elements $T \in \mathcal{R}$ it holds,

$$\widehat{P}(T)\widehat{M}_E\widehat{P}(T^{-1}) = \widehat{M}_E, \quad \forall T \in \mathcal{R}. \quad (10.21)$$

2) See [27] for more details.

Theorem 45 (Group of the master equation). *The group of the master equation, i.e., the group of all transformations that leave the master equation invariant is given by the group of all transformations that leave $\varepsilon(\mathbf{r}_{\parallel})$ invariant (see equation (10.20)).*

Proof. The theorem follows from the invariance of the differential operator $\widehat{M}_E$ under coordinate transformations by rewriting equation (10.21) as

$$\begin{aligned}\widehat{P}(T)\widehat{M}_E\widehat{P}^{-1}(T) &= \widehat{P}(T)\frac{1}{\varepsilon(\mathbf{r}_{\parallel})}\widehat{P}^{-1}(T)\widehat{P}(T)\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right\}\widehat{P}^{-1}(T), \\ &= \frac{1}{\varepsilon(\mathbf{r}_{\parallel})}\widehat{P}(T)\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right\}\widehat{P}^{-1}(T).\end{aligned}\quad (10.22)$$

Thus, one needs to proof that the Laplacian is invariant, i.e.,

$$\widehat{P}(T)\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right\}\widehat{P}^{-1}(T)f(\mathbf{r}) = \left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right\}f(\mathbf{r}) \quad (10.23)$$

holds for all $T \in \mathcal{R}$. To show the invariance under rotations and translations a coordinate transformation is assumed as follows³⁾,

$$\mathbf{r}' = \underline{\underline{R}} \cdot \mathbf{r} + \mathbf{t}, \quad \text{i.e.} \quad r'_j = \sum_{i=1}^2 (R_{ji} r_i + t_i). \quad (10.24)$$

Here, $\underline{\underline{R}}$ and $\mathbf{t}$ denote a rotation and a translation associated with a symmetry element T . It follows from (10.24) that $\partial r'_j / \partial r_i = R_{ji}$. Therefore the Laplacian is invariant under translations of any kind. Furthermore, the left-hand side of (10.23) can be written as

$$\widehat{P}(T) \sum_{i=1}^2 \frac{\partial^2}{\partial r_i^2} \widehat{P}^{-1}(T)f(\mathbf{r}) = \widehat{P}(T) \sum_{i=1}^2 \frac{\partial}{\partial r_i} \frac{\partial}{\partial r_i} f(\mathbf{r}') \quad (10.25)$$

$$= \widehat{P}(T) \sum_{i=1}^2 \frac{\partial}{\partial r_i} \sum_{j=1}^2 R_{ji} \frac{\partial}{\partial r'_j} f(\mathbf{r}') \quad (10.26)$$

$$= \widehat{P}(T) \sum_{k=1}^2 \sum_{j=1}^2 \frac{\partial}{\partial r'_k} \frac{\partial}{\partial r'_j} f(\mathbf{r}') \sum_{i=1}^2 R_{ki} R_{ji}. \quad (10.27)$$

Since rotation matrices are orthogonal ($\underline{\underline{R}}^{-1} = \underline{\underline{R}}^T$) it follows that

$$\sum_{i=1}^2 R_{ki} R_{ji} = \delta_{k,j}. \quad (10.28)$$

By introducing a function

$$h_{kj}(\mathbf{r}') = \frac{\partial}{\partial r'_k} \frac{\partial}{\partial r'_j} f(\mathbf{r}'), \quad (10.29)$$

3) $\mathbf{r} = (r_1, r_2, r_3)$, $\mathbf{r}' = (r'_1, r'_2, r'_3)$ is used.

it is possible to write

$$\hat{P}(T) \sum_{k=1}^2 \sum_{j=1}^2 \frac{\partial}{\partial r'_k} \frac{\partial}{\partial r'_j} f(\mathbf{r}') \underbrace{\sum_{i=1}^2 R_{ki} R_{ji}}_{\delta_{j,k}} = \sum_{j=1}^2 \hat{P}(T) h_{jj}(\mathbf{r}') \quad (10.30)$$

$$= \sum_{j=1}^2 h_{jj}(\mathbf{r}) \quad (10.31)$$

$$= \sum_{j=1}^2 \frac{\partial}{\partial r_j} \frac{\partial}{\partial r_j} f(\mathbf{r}) . \quad (10.32)$$

It can be concluded that the symmetry of the master equation is entirely defined by the symmetry of $\varepsilon(\mathbf{r}_{\parallel})$ and that $\hat{P}(T)\hat{M}_E\hat{P}(T^{-1}) = \hat{M}_E$ is true if and only if $\hat{P}(T)\varepsilon(\mathbf{r}_{\parallel})\hat{P}(T^{-1}) = \varepsilon(\mathbf{r}_{\parallel})$. $\square$

10.3

Master Equation as an Eigenvalue Problem

Due to the symmetry properties of $\varepsilon(\mathbf{r})$ the master equation (10.14) can be evaluated further. Corresponding to the translational invariance of $\varepsilon(\mathbf{r})$, the vector field $\mathbf{H}(\mathbf{r})$ has to be a BLOCH function

$$\mathbf{H}(\mathbf{r} + \mathbf{t}) = e^{i\mathbf{k} \cdot \mathbf{t}} \mathbf{H}(\mathbf{r}) , \quad (10.33)$$

where $\mathbf{t}$ is a primitive lattice vector $\mathbf{t} \in \mathcal{T} \subset \mathcal{R}$. An expansion of $\mathbf{H}(\mathbf{r})$ in terms of plane waves guaranties the validity of (10.33),

$$\mathbf{H}(\mathbf{r}) = \sum_{\mathbf{G}, \lambda} h_{\mathbf{G}}^{\lambda}(\mathbf{k}) \mathbf{e}_{\mathbf{G}}^{\lambda} e^{i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}} , \quad (10.34)$$

where the index λ describes the two independent linear polarizations. The polarization vectors $\mathbf{e}_{\mathbf{G}}^{\lambda}$ are oriented perpendicular to the propagation direction $(\mathbf{k} + \mathbf{G})$ of the plane wave.

$$\mathbf{e}_{\mathbf{G}}^1 = \frac{\mathbf{e}_z \times (\mathbf{k} + \mathbf{G})}{|\mathbf{e}_z \times (\mathbf{k} + \mathbf{G})|} , \quad (10.35)$$

$$\mathbf{e}_{\mathbf{G}}^2 = \frac{\mathbf{e}_{\mathbf{G}}^1 \times (\mathbf{k} + \mathbf{G})}{|\mathbf{e}_{\mathbf{G}}^1 \times (\mathbf{k} + \mathbf{G})|} . \quad (10.36)$$

The ansatz (10.34) transfers the master equation in a homogeneous set of linear equations for the coefficients $h_{\mathbf{G}}^{\lambda}(\mathbf{k})$

$$\sum_{\mathbf{G}, \lambda} \left[M_{\mathbf{G}, \mathbf{G}'}^{\lambda, \lambda'}(\mathbf{k}) - \left(\frac{\omega}{c} \right)^2 \delta_{\lambda, \lambda'} \delta_{\mathbf{G}, \mathbf{G}'} \right] h_{\mathbf{G}}^{\lambda}(\mathbf{k}) = 0 . \quad (10.37)$$

The matrix $M_{\mathbf{G},\mathbf{G}'}^{\lambda,\lambda'}(\mathbf{k})$ is given by

$$M_{\mathbf{G},\mathbf{G}'}^{\lambda,\lambda'}(\mathbf{k}) = |\mathbf{k} + \mathbf{G}| \cdot |\mathbf{k} + \mathbf{G}'| \kappa(\mathbf{G} - \mathbf{G}') \begin{pmatrix} \mathbf{e}_{\mathbf{G}}^2 \cdot \mathbf{e}_{\mathbf{G}'}^2 & -\mathbf{e}_{\mathbf{G}}^2 \cdot \mathbf{e}_{\mathbf{G}'}^1 \\ -\mathbf{e}_{\mathbf{G}}^1 \cdot \mathbf{e}_{\mathbf{G}'}^2 & \mathbf{e}_{\mathbf{G}}^1 \cdot \mathbf{e}_{\mathbf{G}'}^1 \end{pmatrix}. \quad (10.38)$$

$\kappa(\mathbf{G})$ is the FOURIER transform of the inverse permittivity. It contains the variation of the permittivity in the unit cell. A detailed discussion follows in the next section.

Now, a two-dimensional photonic crystal is considered (translational invariant in the z -direction) where the plane waves propagate in the x - y plane. The wave vector $\mathbf{k}_{\parallel}$ and the reciprocal lattice vector $\mathbf{G}_{\parallel}$ correspond to the two-dimensional problem. The polarization vectors $\mathbf{e}_{\mathbf{G}_{\parallel}}^1$ are perpendicular to $\mathbf{e}_z$ while all vectors $\mathbf{e}_{\mathbf{G}_{\parallel}}^2$ are parallel to $\mathbf{e}_z$. Hence, the products $\mathbf{e}_{\mathbf{G}_{\parallel}}^1 \cdot \mathbf{e}_{\mathbf{G}_{\parallel}}^2$ in (10.38) vanish and (10.38) decouples into two separate problems for the TM and TE modes,

$$\sum_{\mathbf{G}_{\parallel}} \left[|\mathbf{k}_{\parallel} + \mathbf{G}_{\parallel}| \cdot |\mathbf{k}_{\parallel} + \mathbf{G}'_{\parallel}| \kappa(\mathbf{G}_{\parallel} - \mathbf{G}'_{\parallel}) - \left(\frac{\omega}{c}\right)^2 \delta_{\mathbf{G}_{\parallel},\mathbf{G}'_{\parallel}} \right] h_{\mathbf{G}_{\parallel}}^{\text{TE}}(\mathbf{k}_{\parallel}) = 0, \quad (10.39)$$

and

$$\sum_{\mathbf{G}_{\parallel}} \left[(\mathbf{k}_{\parallel} + \mathbf{G}_{\parallel}) \cdot (\mathbf{k}_{\parallel} + \mathbf{G}'_{\parallel}) \kappa(\mathbf{G}_{\parallel} - \mathbf{G}'_{\parallel}) - \left(\frac{\omega}{c}\right)^2 \delta_{\mathbf{G}_{\parallel},\mathbf{G}'_{\parallel}} \right] h_{\mathbf{G}_{\parallel}}^{\text{TM}}(\mathbf{k}_{\parallel}) = 0. \quad (10.40)$$

Here, $h_{\mathbf{G}_{\parallel}}^{\text{TE}}(\mathbf{k}_{\parallel})$ and $h_{\mathbf{G}_{\parallel}}^{\text{TM}}(\mathbf{k}_{\parallel})$ denote the associated expansion coefficients.

10.4

Models of the Permittivity

FOURIER transform $\kappa(\mathbf{G})$ of the inverse permittivity $\kappa(\mathbf{r})$	
GTPhSlab	Structure factor of a slab
GTPhEllipticRod	Structure factor of an elliptic rod
GTPhPrismaticRod	Structure factor of a prismatic rod
GTPhSlabSmooth	Structure factor of a slab with a smoothed profile
GTPhRodSmooth	Structure factor of a rectangular rod with a smoothed profile
GTPhCuboid	Structure factor of a cuboid
GTPhSphere	Structure factor of a sphere
GTPhDObjects	$\kappa(\mathbf{G})$ of an arrangement of objects in the unit cell for $\mathbf{G}$
GTPhShowStructure	Shows the arrangement of the objects in the unit cell
GTPhDCPixel	$\kappa(\mathbf{G})$ of a pixel map for $\mathbf{G}$
GTPhPixelSmooth	Smoothing of a pixel map
GTPhPixelStructure	Modification and plot of $\kappa(\mathbf{r})$ defined as a pixel map
GTPhPixelSmooth	Smoothing of a pixel map
GTPhPermittivityMatrix	Calculates $\kappa(\mathbf{G}, \mathbf{G}')$

The FOURIER transform of the inverse permittivity $\kappa(\mathbf{r}) = \varepsilon^{-1}(\mathbf{r})$ in (10.38) is defined as

$$\kappa(\mathbf{G}) = \frac{1}{V_0} \int_{V_0} \kappa(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} d^d \mathbf{r}. \quad (10.41)$$

In (10.41) d is the space dimension, V_0 is the volume of the unit cell, and $\mathbf{G}$ and $\mathbf{r}$ are reciprocal lattice and position vectors with corresponding space dimension, respectively. Dielectric stacks, two-dimensional and three-dimensional photonic crystals correspond to the dimensions $d = 1, 2, 3$.

Equation (10.41) can be evaluated analytically, if the spatial variation of $\varepsilon(\mathbf{r})$ is represented by simple geometric objects. In the following, the discussion concentrates on the two-dimensional case. It is assumed that the permittivity in the unit cell consists of N patches. Each patch i has an area A_i and the permittivity ε_i , which is assumed to be constant within the patch (cf. Figure 10.2). The patches play the role of *dielectric atoms*. Introducing the functions

$$A_i(\mathbf{r}) = \begin{cases} 1 & \mathbf{r} \in A_i \\ 0 & \mathbf{r} \notin A_i \end{cases}, \quad i = 1, \dots, N, \quad (10.42)$$

the unit cell area A_0 can be expressed as

$$A_0 = \sum_{i=1}^N \int_{A_0} A_i(\mathbf{r}) d^2 \mathbf{r} = \sum_{i=1}^N A_i. \quad (10.43)$$

Usually, one of the patches is defined as the dielectric background, which is patch 5 in the example of Figure 10.2. The choice of the background material is motivated by physical reasoning. The inverse permittivity in the unit cell can be expressed by means of $A_i(\mathbf{r})$ (10.42) as

$$\kappa(\mathbf{r}) = \sum_{i=1}^N \kappa_i A_i(\mathbf{r}). \quad (10.44)$$

The evaluation of (10.41) with (10.44) results in

$$\kappa(\mathbf{G}) = \sum_{i=1}^N \kappa_i \left(\frac{A_i}{A_0} \right) \left[\frac{1}{A_i} \int_{A_i} A_i(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} d^2 \mathbf{r} \right]. \quad (10.45)$$

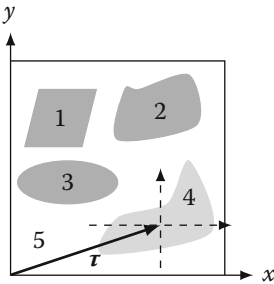


Figure 10.2 Distribution of ε in a square unit cell. The permittivity is constant within each of the $N = 5$ patches. Local coordinate systems are used for each individual patch.

The quantity $\gamma_i = A_i/A_0$ is the so-called *filling factor* of the i th patch. The *structure factor* $S_i(\mathbf{G})$ of the i th patch is fully defined by its geometry and given by

$$S_i(\mathbf{G}) = \frac{1}{A_i} \int_{A_0} A_i(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} d^2 \mathbf{r} . \quad (10.46)$$

Hence, the FOURIER transform of the inverse permittivity is expressed as

$$\kappa(\mathbf{G}) = \sum_{i=1}^N \kappa_i \gamma_i S_i(\mathbf{G}) . \quad (10.47)$$

In the case of $\mathbf{G} = 0$, the structure factor simplifies to $S_i(\mathbf{G}) = 1$ and (10.47) results in

$$\kappa(0) = \sum_{i=1}^N \kappa_i \gamma_i = \frac{1}{A_0} \sum_{i=1}^N \kappa_i A_i . \quad (10.48)$$

It follows that $\kappa(0)$ represents the mean value of $\kappa(\mathbf{r})$ in the unit cell. Selecting one patch as the background material, equation (10.48) can be written as

$$\kappa(0) = \kappa_b + \sum_{i=1}^{N-1} (\kappa_i - \kappa_b) \gamma_i \quad (10.49)$$

$$\kappa(0) = \kappa_b + \gamma(\kappa - \kappa_b) = \gamma\kappa + (1 - \gamma)\kappa_b \quad (N = 2) , \quad (10.50)$$

where κ_b denotes the inverse permittivity for the background material. The problem is now formulated in terms of a dielectric contrast with respect to the background material. For $\mathbf{G} \neq 0$, it follows

$$\kappa(\mathbf{G}) = \sum_{i=1}^{N-1} (\kappa_i - \kappa_b) \gamma_i S_i(\mathbf{G}) . \quad (10.51)$$

According to (10.46), the structure factor $S_i(\mathbf{G})$ is defined with respect to the position of the dielectric atom in the unit cell. The analytic form of the structure factor can be calculated within an appropriate local frame of coordinates. Figure 10.3 shows a transformation of a prismatic rod incorporating a shift with respect to the unit cell frame and a rotation with respect to the coordinate system used for the analytic calculation. Using the transformation $\mathbf{r} = \mathbf{r}' + \boldsymbol{\tau}$, the calculation of the structure factor can be performed in the $x'-y'$ coordinate system.

$$\begin{aligned} S_i(\mathbf{G}) &= \frac{1}{A_i} \int_{A_0} A_i(\boldsymbol{\tau} + \mathbf{r}') e^{-i\mathbf{G}\cdot(\boldsymbol{\tau} + \mathbf{r}')} d^2 \mathbf{r}' , \\ &= e^{-i\mathbf{G}\cdot\boldsymbol{\tau}} \left(\frac{1}{A_i} \int_{A_0} \overline{A}_i(\mathbf{r}') e^{-i\mathbf{G}\cdot\mathbf{r}'} d^2 \mathbf{r}' \right) = e^{-i\mathbf{G}\cdot\boldsymbol{\tau}} \overline{S}_i(\mathbf{G}) . \end{aligned} \quad (10.52)$$

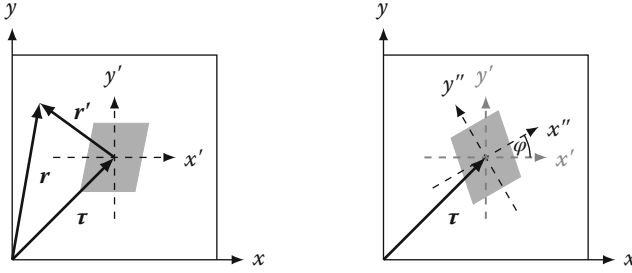


Figure 10.3 A prismatic rod in general position in the unit cell. It is shifted with respect to the unit cell frame and rotated with respect to its standard orientation in the $x'-y'$ coordinate system.

By performing a rotation mediated by the rotation matrix $\underline{\underline{R}}$ with respect to the standard coordinate frame, i.e., $\mathbf{r}'' = \underline{\underline{R}}\mathbf{r}'$, the corresponding structure factor can be derived via $\bar{S}_i(\underline{\underline{R}}\mathbf{G})$. In general, only the reduced structure factors $\bar{S}_i(\mathbf{G})$ have to be known for the construction of the analytic form of the FOURIER transform of the inverse permittivity for an ensemble of objects in the unit cell,⁴⁾

$$\kappa(\mathbf{G}) = \sum_{i=1}^{N-1} (\kappa_i - \kappa_b) \gamma_i e^{-i\mathbf{G} \cdot \mathbf{r}} \bar{S}_i(\underline{\underline{R}}\mathbf{G}). \quad (10.53)$$

The method developed so far can be extended to approximate an arbitrary distribution of the permittivity in the unit cell, where the reduced structure factor of the prismatic rod is the basic element to define the distribution $\varepsilon(\mathbf{r})$ in the unit cell by means of a pixel map. For example, the rhomboidal unit cell of side lengths a, b and angle φ can be divided into $N_p = N_a N_b$ pixels. The filling factor of each pixel is given by

$$\gamma = (N_a N_b)^{-1} \quad (10.54)$$

The pixel map $\varepsilon_{i,j}$, $i = 1, \dots, N_a$, $j = 1, \dots, N_b$ describes the distribution of the permittivity within the unit cell. Within this model $\kappa(\mathbf{G})$ is given by

$$\kappa(0) = \frac{1}{N_p} \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} \frac{1}{\varepsilon_{i,j}}, \quad (10.55)$$

$$\kappa(\mathbf{G}) = \frac{\bar{S}(\mathbf{G})}{N_p} \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} \frac{1}{\varepsilon_{i,j}} e^{-i\mathbf{G} \cdot \mathbf{r}_{i,j}}, \quad (10.56)$$

where $\bar{S}(\mathbf{G})$ denotes the structure factor of one pixel. The method can be used to optimize photonic band gaps employing genetic algorithms [178]. Within GTPack, the commands **GTPhPixelStructure** and **GTPhShowStructure** allow one to visualize the distribution of $\varepsilon(\mathbf{r})$ in the unit cell of a model under consideration. An example is shown in Figure 10.4.

4) It is not the aim of this consideration to find the most effective numerical method for a photonic band structure calculation.

Mathematica**GTPhPixelStructure, GTPhShowStructure**

```

A permittivity map of a circular rod with varying permittivity in the center of a square unit cell is defined.

In[22]:= pixelmap = Table[rad = Norm[(i - 21)^2 + (j - 21)^2] / 20;
  If[rad < 10, 15 - rad, 1], {i, 1, 41}, {j, 1, 41}]; struct = {1, 1, π/2};
gpxel = GTPhPixelStructure[pixelmap, {}, struct, GOCOLORScheme -> "SolarColors"];
Structures in a rhomboidal unit cell are defined.

In[23]:= structures = {{{"CircularRod", 12, {.5, .1}, {0, 0, 0}},
  {"EllipticRod", 5, {0.03, .05, .2, π/6}, {.7, .7, 0}},
  {"RectangularRod", 7, {.5, .2, .1, π/4}, {0.2, -.6, 0}},
  {"PrismaticRod", 4, {.5, .2, .3, π/6, 0}, {0, .3, 0}}};
basis = {{1, 0, 0}, {Cos[π/3], Sin[π/3], 0}}; gstructures =
  GTPhShowStructure[structures, 2, basis, 2, GOCOLORScheme -> "SolarColors"];

In[24]:= Grid[{gpxel, gstructures}]

```

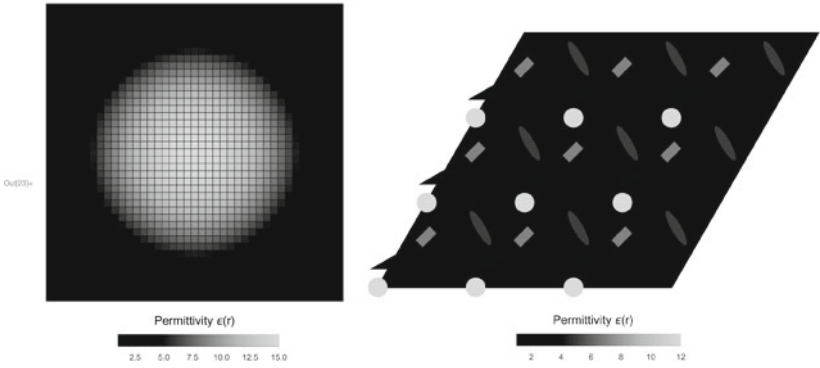


Figure 10.4 Definition of $\epsilon(r)$ by means of a pixel map or an ensemble of objects in the unit cell.

10.4.1

Reduced Structure Factors

According to (10.53), only the reduced structure factors

$$\bar{S}_i(\mathbf{G}) = \frac{1}{A_i} \int_{V_0} \bar{A}_i(\mathbf{r}') e^{-i\mathbf{G} \cdot \mathbf{r}'} d^d \mathbf{r}', \quad (10.57)$$

calculated in an appropriate coordinate system, have to be known to construct the FOURIER transforms of the inverse permittivity. Subsequently, analytic results for simple geometric objects are summarized. The functions $J_n(z)$ denote BESSEL functions of the first kind and $j_n(z)$ denote spherical BESSEL functions of the first kind, respectively.

- **Dielectric slab** ($|x| \leq a/2$)

$$\bar{S}(G) = j_0\left(\frac{Ga}{2}\right) \quad (10.58)$$

The reference point is the middle of the slab.

- **Prismatic rod**

Assume a rod having the side lengths a, b , where side a is oriented parallel to the x -axis. The angle between both sides is denoted by α .

$$\bar{S}(\mathbf{G}) = j_0 \left(\frac{G_x a}{2} \right) j_0 \left(\frac{b}{2} (G_x \cos \alpha + G_y \sin \alpha) \right) \quad (10.59)$$

The reference point is the intersection of the diagonals. For a rectangular rod it follows

$$\bar{S}(\mathbf{G}) = j_0 \left(\frac{G_x a}{2} \right) j_0 \left(\frac{G_y b}{2} \right). \quad (10.60)$$

- **Elliptical rod**

Photonic crystals can be produced, e.g., by electrochemical etching of pores in silicon (cf. BIRNER *et al.* [179]). The etching process can be controlled such that azimuthal etching variations (variation of the thickness) of the pores can be incorporated with high accuracy. To quantify such variations the influence of orientational variations and the eccentricity of the pores were studied in great detail [180, 181]. An elliptical rod with the major axis a_e in the x -direction and the minor axis b_e in the y -direction is assumed. The structure factor is given by

$$\bar{S}(\mathbf{G}) = 2 \frac{J_1(b_e \sqrt{g})}{b_e \sqrt{g}}, \quad g = G_x^2 + \left(\frac{a_e}{b_e} \right) G_y^2 \quad (10.61)$$

The reference point is the center of the ellipse.

- **Circular rod** of radius r_s :

For the circular rod ($a_e = b_e = r_s$) equation (10.61) simplifies to

$$\bar{S}(\mathbf{G}) = 2 \frac{J_1(|\mathbf{G}| r_s)}{|\mathbf{G}| r_s}. \quad (10.62)$$

- **Sphere** of radius r_s :

The reduced structure factor for a sphere is given by

$$\bar{S}(\mathbf{G}) = 3 \frac{j_1(|\mathbf{G}| r_s)}{|\mathbf{G}| r_s}. \quad (10.63)$$

The reference point is given by the center of the sphere.

- **Cuboid** ($|x| < a/2, |y| < b/2, |z| < c/2$):

In accordance with the results for the slab and the rectangular rod, the reduced structure factor for the cuboid is given by

$$\bar{S}(\mathbf{G}) = j_0 \left(\frac{G_x a}{2} \right) j_0 \left(\frac{G_y b}{2} \right) j_0 \left(\frac{G_z c}{2} \right). \quad (10.64)$$

Task 36 (Definition of $\varepsilon(\mathbf{r})$ using pixel maps.). In Figure 10.4, it is shown how pixel maps can be used to represent arbitrary structures in a two-dimensional cell. Analytical expression for the permittivity $\varepsilon(\mathbf{r})$ are implemented for elliptic rods and prismatic rods. Generate elliptic and prismatic rods from pixel maps and depict the structures by means of **GTPhPixelStructure**.

10.4.2

Convergence of the Plane Wave Expansion

Because of the smooth character of the crystal potential only a few FOURIER components of the potential are necessary in the calculation of a model band structure of a nearly free electron metal or a semiconductor. The step-like behavior of the permittivity in a photonic crystal, however, leads to a large number of plane waves in the plane wave expansion of the electromagnetic fields. As discussed at the beginning of this chapter the patches of constant permittivity in the unit cell are described by the functions $A_i(\mathbf{r})$ introduced in equation (10.42). For a dielectric slab this function is given by

$$A(x) = \Theta\left(x + \frac{d}{2}\right) + \Theta\left(x - \frac{d}{2}\right) \quad (10.65)$$

A smoothed profile can be generated by the convolution of (10.65) with a Gaussian characterized by the variance σ^2 ,

$$\bar{A}(x) = \frac{1}{2} \left[\operatorname{erf}\left(\frac{d/2 + x}{\sqrt{2}\sigma}\right) + \operatorname{erf}\left(\frac{d/2 - x}{\sqrt{2}\sigma}\right) \right] \quad (10.66)$$

The reduced structure factor

$$\bar{S}(G) = \frac{1}{a} \int_{-a/2}^{+a/2} dx \bar{A}(x) e^{-Gx} \quad (10.67)$$

of the slab can be calculated analytically by means of *Mathematica*.⁵⁾

The FOURIER coefficients $\kappa(\mathbf{G})$ follow from the structure factors corresponding to (10.49)–(10.51). From Figure 10.5, it can be seen that in the case of a smoothed profile, the coefficients $\kappa(G)$ do not show long-range oscillations. The profile of the permittivity $\varepsilon(\mathbf{r})$ can be reconstructed from the coefficients $\kappa(\mathbf{G})$ by means of

$$\frac{1}{\varepsilon(\mathbf{r})} = \sum_{\mathbf{G}} \kappa(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}}. \quad (10.68)$$

Figure 10.5 demonstrates that by expanding the stepped profile in terms of plane waves, the so-called GIBBS phenomenon can be observed, i.e., the FOURIER series

5) The analytic result is implemented in the modules **GTPhSlabSmooth** and **GTPhRodSmooth**.

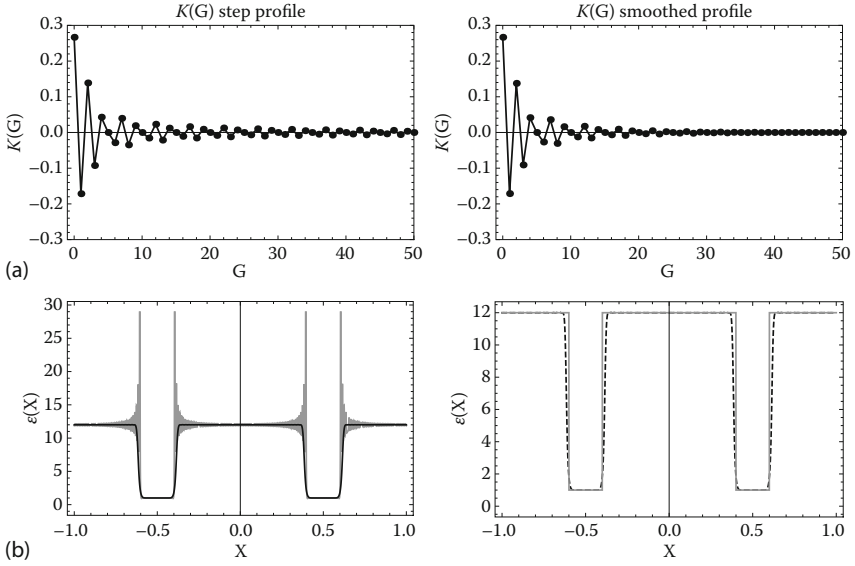


Figure 10.5 Comparison of a FOURIER expansion for a smoothed and a nonsmoothed profile of the permittivity. (a) FOURIER coefficients of a slab with filling factor $\gamma = 0.8$ and a permittivity of $\varepsilon_s = 12$ of the slab and a background value $\varepsilon_b = 1$. The full width at half-maximum of the Gaussian is

$\sigma = 0.01$. (b) Left: Number of plane waves $N_G = 201$ for the stepped $\varepsilon(r)$ -profile (gray) but $N_G = 101$ for the smoothed profile (black solid line). Right: Comparison of the stepped profile with the smoothed profile ($\gamma = 0.8$, $\varepsilon_s = 12$, $\varepsilon_b = 1$, $\sigma = 0.01$).

shows large oscillations near the jump. If the smoothed function $\bar{A}(x)$ is used for the calculation of the FOURIER coefficients $\kappa(\mathbf{G})$, these oscillations are removed in large part. In this case, a much smaller number of plane waves leads to a better reconstruction of the original profile.

11

Two-Dimensional Photonic Crystals

...das Schwerste an dieser Entdeckungsfahrt war sicher der Entschluss, alles bisher bekannte Land zu verlassen und so weit nach Westen zu segeln, dass mit den vorhandenen Vorräten eine Umkehr nicht mehr möglich war. In ähnlicher Weise kann wirkliches Neuland in einer Wissenschaft wohl nur gewonnen werden, wenn man an einer entscheidenden Stelle bereit ist, den Grund zu verlassen, auf dem die bisherige Wissenschaft ruht, und gewissermaßen ins Leere zu springen.

Werner Heisenberg
(*Der Teil und das Ganze*, Piper-Verlag, 1972)

During the chapter, several examples of two-dimensional photonic crystals are discussed. For these examples, the photonic band structure is obtained by solving the respective master equations. Additionally, the photonic band structure is investigated with respect to the underlying symmetry. Here, the bands can be associated with the irreducible representations of the group of the master equation. The chapter starts with an empty lattice calculation, where the free linearly dispersing photonic band is backfolded at the Brillouin zone boundaries. Second, cylindric rods within a square lattice are discussed. For this example, so-called photonic band gaps, i.e., frequency ranges, where the light propagation is suppressed can be found for the transverse magnetic mode. Furthermore, examples are given, where degeneracies within photonic band structures can be lifted by symmetry breaking. Finally, defect modes are discussed which arise for defects within the photonic crystals. Similar to electronic defect states, such defect modes can occur within the photonic band gap of a photonic crystal.

11.1

Photonic Band Structure and Symmetrized Plane Waves

Photonic band structures	
GTPhMaster	Gives the master equation for a given $\kappa(\mathbf{G}, \mathbf{G}')$
GTPhMasterObjects	Gives the master equation for a given list of geometrical objects
GTPhMasterPixel	Gives the master equation for a given pixel map of the permittivity
GTPhMPBBands	Reads a photonic band structure calculated by MPB
GTPwEmptyLatticeRep	Gives the irreducible representations for the empty lattice bands

The calculation and analysis of photonic band structures (PBS) and eigenmodes is based on the formulation of the master equation in terms of an eigenvalue problem (cf. Section 10.3). The inverse permittivity and its FOURIER transform $\kappa(\mathbf{G})$, which represents the central quantity in this equation, was discussed in Section 10.4. Within GTPack three different methods to solve the master equation for two-dimensional systems are implemented, which will be presented subsequently. In the case where the analytic form of $\kappa(\mathbf{G})$ for objects within the elementary cell is known, the command **GTPhMasterObjects** can be applied. Geometrically more complicated objects can be approximated by a pixel map (where $\kappa(\mathbf{G})$ is analytically known for each pixel). This case is covered by the command **GTPhMasterPixel**. In both methods, the coefficients $\kappa(\mathbf{G}, \mathbf{G}')$ are calculated during the setup of the eigenvalue problem. However, it is also possible to calculate the matrix beforehand using **GTPhPermittivityMatrix**. The eigenvalue problem itself can be constructed afterwards with the help of **GTPhMaster**.

11.1.1

Empty Lattice Band Structure and Symmetrized Plane Waves

The so-called empty lattice test serves as a starting point for the discussion of periodic dielectric structures. It is assumed that the permittivity is given by $\varepsilon(\mathbf{r}) = 1$. Additionally, the system preserves the lattice periodicity, i.e., the free photon dispersion $\omega = c \cdot k$ is folded into the first BRILLOUIN zone in the reduced zone scheme. According to equation (10.41), the Fourier transform of the inverse permittivity $\kappa(\mathbf{G}_{\parallel})$ is given by

$$\kappa(\mathbf{G}_{\parallel}) = \delta_{\mathbf{G}_{\parallel}, 0}. \quad (11.1)$$

The two polarization states become indistinguishable, and it follows that (10.39) and (10.40) are equivalent,

$$\sum_{\mathbf{G}_{\parallel}} \left[(\mathbf{k}_{\parallel} + \mathbf{G}_{\parallel}) \cdot (\mathbf{k}_{\parallel} + \mathbf{G}'_{\parallel}) - \left(\frac{\omega}{c} \right)^2 \right] h_{\mathbf{G}_{\parallel}}(\mathbf{k}_{\parallel}) \delta_{\mathbf{G}_{\parallel}, \mathbf{G}'_{\parallel}} = 0. \quad (11.2)$$

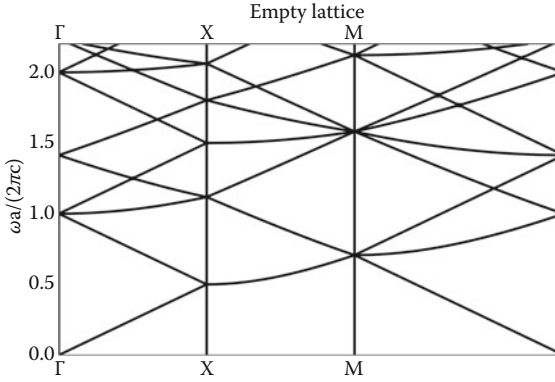


Figure 11.1 Empty lattice photonic band structure for a square lattice.

Because of the δ -distribution, the master equation becomes an eigenvalue problem of a diagonal matrix. Introducing dimensionless variables¹⁾

$$\mathbf{k}_{\parallel} = \tilde{\mathbf{k}}_{\parallel} \frac{2\pi}{a}, \quad \mathbf{G}_{\parallel} = \tilde{\mathbf{G}}_{\parallel} \frac{2\pi}{a}, \quad \omega = \tilde{\omega} \frac{2\pi c}{a} \rightarrow \tilde{\omega} = \frac{\omega a}{2\pi c} \quad (11.3)$$

equation (11.2) can be written as

$$\sum_{\tilde{\mathbf{G}}_{\parallel}} \left[(\tilde{\mathbf{k}}_{\parallel} + \tilde{\mathbf{G}}_{\parallel}) \cdot (\tilde{\mathbf{k}}_{\parallel} + \tilde{\mathbf{G}}'_{\parallel}) - \tilde{\omega}^2 \right] h_{\tilde{\mathbf{G}}_{\parallel}}(\tilde{\mathbf{k}}_{\parallel}) \delta_{\tilde{\mathbf{G}}_{\parallel}, \tilde{\mathbf{G}}'_{\parallel}} = 0. \quad (11.4)$$

Using $\tilde{\mathbf{k}}_{\parallel} = (\xi, \eta, \zeta)$ and $\tilde{\mathbf{G}}_{\parallel} = (\tilde{G}_x, \tilde{G}_y, \tilde{G}_z)$ the band structure can be calculated from equation (11.4). It follows that the photon dispersion relation is given by

$$\tilde{\omega} = |\tilde{\mathbf{k}}_{\parallel} + \tilde{\mathbf{G}}_{\parallel}| = \left[(\xi + \tilde{G}_x)^2 + (\eta + \tilde{G}_y)^2 + (\zeta + \tilde{G}_z)^2 \right]^{1/2}. \quad (11.5)$$

The empty lattice band structure for a two-dimensional square lattice is shown in Figure 11.1. The linear dispersion of the bands emerging from the Γ point and the back-folding on the BRILLOUIN zone boundary can be verified nicely.

Task 37 (Empty lattice band structures). Calculate the empty lattice band structures for the fcc and bcc lattice by means of GTPack commands. Compare the results with analytical expressions for the bands.

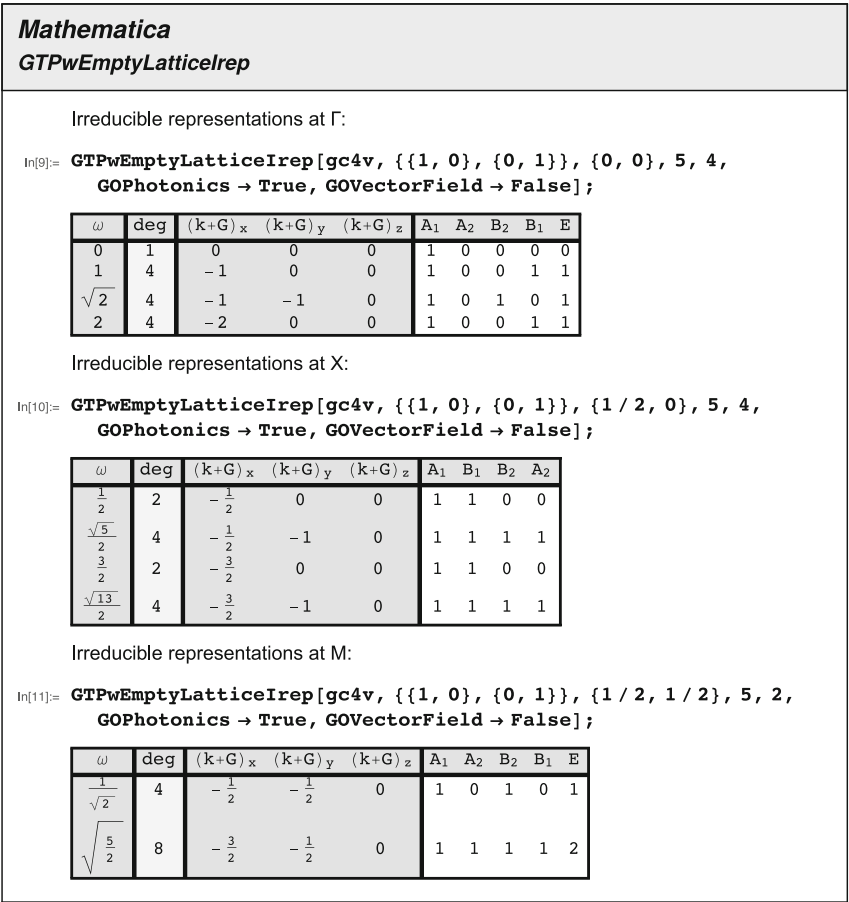
The irreducible representations corresponding to the highly degenerate levels of the empty lattice band structure can be estimated using **GTPwEmptyLatticeRep**. The application of **GTPwEmptyLatticeRep** is restricted to symmetric space groups. Within the command, the group of the wave vector $\mathcal{G}_0(\mathbf{k})$ is determined

1) Reduced units are used in the photonics part of GTPack for numerical calculations. The difference between quantities and their reduced counterparts is mostly obvious, i.e., in the discussion the special notation of reduced quantities is suppressed.

and the corresponding character table is calculated. The vectors $(\mathbf{G}_i + \mathbf{k})$, where $\mathbf{G}_i$ are the reciprocal lattice vectors, are sorted in shells with respect to $|\mathbf{G}_i + \mathbf{k}|$. The eigenmode frequency $\omega_\nu(\mathbf{k})$ corresponding to the ν th shell is estimated and the number of vectors within the shell determines the degeneracy of the level. A characteristic vector of the corresponding shell is also presented.

Since bands along the symmetry lines might also be degenerate, the degeneracy of the levels in general cannot be concluded from a band structure picture like Figure 11.1. For example, the third band along the path ΓX (Δ -line) is twofold degenerate. Therefore, the level $\omega_2(\Gamma) = 1$ has a degeneracy of 4.

The vectors of a shell are used as a basis to construct a faithful representation of $G_0(\mathbf{k})$. In general, this representation is reducible and can be reduced with respect to the irreducible representations of $G_0(\mathbf{k})$.



Example 56 (Irreducible representations for the empty lattice band structure of a square lattice). The application of **GTPwEmptyLatticeRep** to the empty lattice band structure of a square lattice is shown in Figure 11.2. For an empty lattice band structure, the symmetry of the underlying lattice is introduced artificially. In general, the degeneracy of the energy levels correspond to an irreducible representation of the group of all rotations and translations in the two-dimensional space. Clearly, this representation is reducible for the symmetry of the lattice under consideration, e.g., the square lattice. Thus, several irreducible representations of the two-dimensional space group might correspond to the same energy level. The space group of the square lattice is symmorphic, i.e., **GTPwEmptyLatticeRep** can be used to estimate the irreducible representations that occur at a certain **k**-point.

The construction of symmetry adapted plane waves was already discussed in Section 9.3.1 and will not be repeated here.

11.1.2

Photonic Band Structures: A First Example

As an example, the photonic band structure of a two-dimensional square lattice of circular alumina rods ($\epsilon = 8.9$) in air is discussed, where the radius of the rods is given by $R = 0.2a$ (a – lattice constant). This corresponds to a filling factor of $\gamma = 0.126$. A propagation of light perpendicular to the rods is considered.

A band structure calculated using the MIT Photonic Bands package (MPB) [174, 175] for both, the TE and the TM mode, is shown in Figure 11.3. The command **GTMPBBands** serves as an interface between MPB and GTPack and is used to read the MPB data in an appropriate form.²⁾

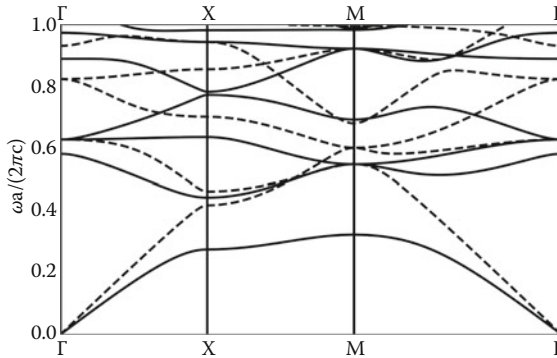


Figure 11.3 Photonic band structures of circular rods of alumina ($\epsilon = 8.9$, $R = 0.2a$) in a square lattice calculated using MPB. TE – dashed line, TM modes – solid line.

2) See Appendix C for details about the interaction of MPB and GTPack.

As can be verified, there is no frequency range within the band structure where propagation of light is forbidden, i.e., there is no photonic band gap. However, both individual modes might show gaps. For example, the TM polarization shows a gap between the first and the second band ($0.323 < \tilde{\omega} < 0.442$). A small gap also exists between the fourth and fifth band at X . A more detailed discussion of the symmetry properties is postponed to Section 11.2.

A similar calculation for the TM polarization using GTPack is shown in Figure 11.4. The photonic band structure is calculated from the analytic form of $\kappa(\mathbf{G})$ and in a second calculation from a pixel map. For the approximation of the system via a pixel map, the unit cell is divided into 225 pixels, where the rod itself is represented by 29 pixels. The resulting filling factor of $\gamma = 0.1289$ is close to the exact filling factor of $\gamma = 0.126$ mentioned above. However, because of the approximation, small deviations can be verified in comparison to the use of an exact modeling of a rod. During the calculation, a rather small number of 149 reciprocal lattice vectors is used. Nevertheless, qualitatively, the result agrees well with the MPB calculation shown in Figure 11.3. Increasing the number of plane waves from 149 to 901 decreases the deviations in comparison to the MPB calculation as shown in Figure 11.5). The MPB result was obtained using a tolerance of 10^{-7} .

Task 38 (Calculation with MPB). The calculations of photonic band structures by means of MPB and GTPack are compared in Section 11.1.2. Repeat the calculation with both methods. Details of the application of MPB are given in Appendix C.1. Calculate also the density of states using MPB in combination with GTPack.

Task 39 (Approximate calculation of photonic band structures). In Task 36 it was demonstrated, how pixel maps can be defined to represent a special $\varepsilon(\mathbf{r})$ distribution in the unit cell. A square lattice will be considered. The dielectric object is a square rod (filling factor $\gamma = 0.25$, $\varepsilon = 4.0$) in air. Use 149 plane waves for the GTPack calculation. This is enough for a reasonable agreement with MPB.

1. Use the analytical representation for $\kappa(\mathbf{r})$ and calculate the photonic band structure. Consider the position of the rod at lattice points and in the center of the cell. Proof that the band structure is independent of this choice.
2. Use a mesh of 20×20 pixels in a pixel map. Locate the square rod at the lower left corner of the unit cell. Compare the result with the previous calculations.
3. Distribute a quarter of the dielectric material in form of square rods at the corners of the unit cell. Proof that you get again the same photonic band structure.

Mathematica**GTPhMasterObjects, GTPhMasterPixel**

Definition of the structure as an object.

```
In[8]:= ra = 0.2;
structure = {{ "CircularRod", 8.9, { $\pi$  ra^2, ra, ra, 0, 0}, {0, 0, 0}}};
basvec = {{1, 0}, {0, 1}};
eback = 1;
```

Definition of the reciprocal lattice and construction of the eigenvalue problem.

```
In[10]:= clat = GTLatCluster[basvec, 7];
gvec = GTLatShells[clat, GOSort -> True];
hmobj = GTPhMasterObjects[structure, eback, gvec, GOPhPol -> "TM"];
149 lattice vectors
structures in elementary cell: {CircularRod}
Dimensionality: 2
```

Define the path in the BZ and calculate the photonic band structure.

```
In[12]:= kp = GTBZPath["SquareLattice"]; kpts = GTBZLines[kp, {15, 15, 15}];
bands = GTBands[hmobj, kpts, 10, GOPhotonic -> True];
```

Define the structure as a pixel map.

```
In[14]:= npix = 15; rad = 3; map = Table[1, {npix}, {npix}];
Do[Do[d = Sqrt[(i - (npix + 1)/2.)^2 + (j - (npix + 1)/2.)^2];
If[d ≤ rad, map[[i, j]] = 8.9, None]
, {i, 1, npix}], {j, 1, npix}]
```

Construct the eigenvalue problem from the pixel map and calculate the band structure.

```
In[16]:= basis = {{1, 0, 0}, {0, 1, 0}};
hpixel = GTPhMasterPixel[gvec, map, basis, GOPhPol -> "TM"];
bpixel = GTBands[hpixel, kpts, 10, GOPhotonic -> True];
```

Plot both band structures

```
In[19]:= objects = GTBandsPlot[bands, 10, FrameLabel -> {"", " $\omega$  a / (2  $\pi$  c)"},
PlotLabel -> "TM polarization", Joined -> True,
PlotRange -> {{0, 1.70711}, {0, 1}}, PlotStyle -> Black];
pixel = GTBandsPlot[bpixel, 10, FrameLabel -> {"", " $\omega$  a / (2  $\pi$  c)"},
PlotLabel -> "TM polarization (Comparison of methods)",
Joined -> True, PlotRange -> {{0, 1.70711}, {0, 1}},
PlotStyle -> {{Black, Dashed}}];
Show[pixel, objects]
Maximum Abscissa = 1.70711
Maximum Abscissa = 1.70711
```

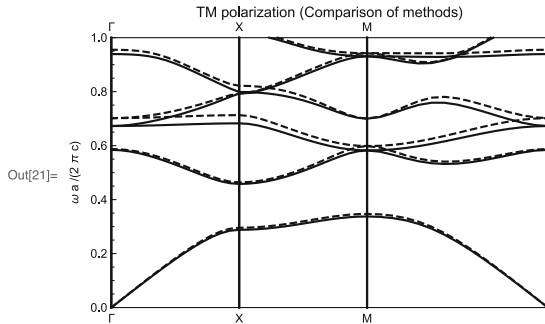


Figure 11.4 Calculation of photonic band structures for dielectric rods in air using the analytic form of $\kappa(\mathbf{G})$ (solid line) and a definition of $\epsilon(\mathbf{r})$ by means of a pixel map (dashed line).

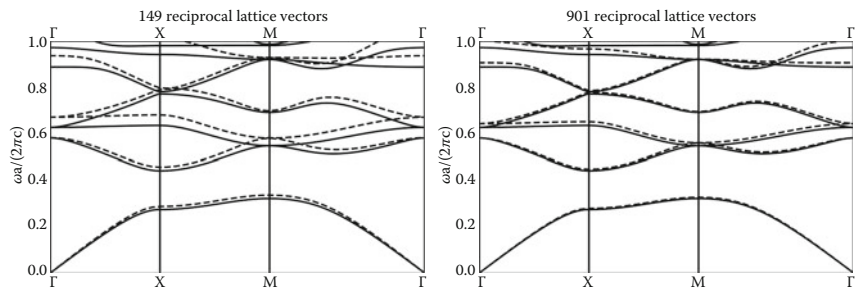


Figure 11.5 Comparison of the photonic band structures for dielectric rods in air calculated by MPB (solid line) and GTPack (dashed line) for different numbers of reciprocal lattice vectors.

11.2

Group Theoretical Classification of Photonic Band Structures

Symmetry analysis of eigenmodes	
GTPhSymmetryBands	Analysis of a complete photonic band structure
GTPhSymmetryField	Analysis of a single eigenmode
GTPhSymmetryPoint	Analysis of all eigenmodes at a $\mathbf{k}$ -point in the BZ
GTBandsPlotImprove	Improve positions of the labels in a band structure plot
GTPhFields	Calculate eigenmode in GTPack
GTPhMPBFields	Read eigenmodes calculated by MPB

In the following, the classification of photonic band structures with respect to the irreducible representations related to the underlying symmetry group is discussed. For simplicity, symmorphic space groups are considered.³⁾ The method presented subsequently is based on the symmetry analysis of the eigenmodes. Within GTPack, eigenmodes can be either imported from MPB calculations by means of **GTPhMPBFields** or calculated in parallel to a photonic band structure calculation using **GTPhFields**.

For TM polarization, the eigenmodes belonging to the ν th band are denoted by $E_{\nu,\mathbf{k}}^z(x, y)$. Similarly to the wave functions belonging to an electronic band structure, the mode $E_{\nu,\mathbf{k}}^z(x, y)$ is a basis function of an irreducible representation of the group of the wave vector $\mathbf{k}$. As introduced in Section 5.4, the application of the character projection operator $\hat{P}^p$, belonging to the irreducible representation Γ^p , to a basis function ϕ_m^q , $m = 1, \dots, l_p$ of an irreducible representation Γ^q gives rise to a nonzero contribution if and only if $p = q$. Hence, in terms of the eigenmodes $E_{\nu,\mathbf{k}}^z(x, y)$ it follows that $\hat{P}_{\mathbf{k}}^p E_{\nu,\mathbf{k}}^z(x, y) \neq 0$ if and only if $E_{\nu,\mathbf{k}}^z(x, y)$ is a basis function of the irreducible representation $\Gamma_{\mathbf{k}}^p$ of the group of the wave vector $\mathbf{k}$. The scheme of applying the character projection operator to the eigenmodes of a photonic band structure calculation is implemented within GTPack. The analysis

3) The approach can be generalized to nonsymmorphic space groups in a similar manner.

can be done for a complete photonic band structure (**GTPHSymmetryBands**), for a single eigenmode (**GTPHSymmetryField**), or for all eigenmodes at a certain **k**-point within the BRILLOUIN zone (**GTPHSymmetryPoint**).

Example 57 (Symmetry analysis of photonic band structures). The example refers to the photonic band structure calculation of a square lattice of dielectric alumina rods in air presented in Section 11.1.2. According to the band structure shown in Figure 11.3, a degeneracy between the second and third band at the M point can be seen. This degeneracy is related to the two-dimensional irreducible representation E of the point group C_{4v} which is the point group the M point is invariant under. An application of **GTPHSymmetryField** to investigate the symmetry of these eigenmodes reveals this assumption, as shown in Figure 11.6. The

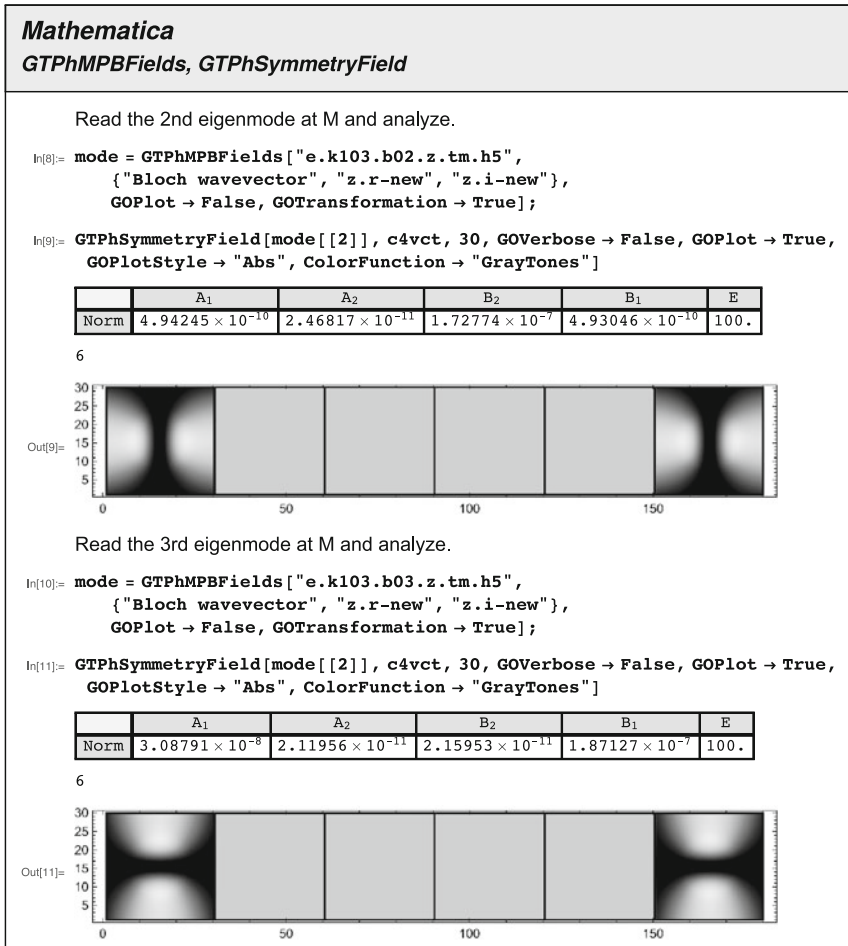


Figure 11.6 Determination of the symmetry of the second and third band at the M point of the photonic band structure of dielectric alumina rods shown in Figure 11.3.

Mathematica
GTPhSymmetryBands

Analysis of the entire band structure.

```
In[8]:= GTPhSymmetryBands["bandstructure_TM", "e.k01.b01.z.tm.h5",
  {{1, "Γ"}, {52, "X"}, {103, "M"}, {154, "Γ"}}, 1, 8,
  {"z.r-new", "z.i-new"}, 30, c4v, {{1, 0}, {0, 1}},
  GOVerbose → False, PlotStyle → {{Thin, Black}},
  Joined → True, PlotRange → {{0, 1.82}, {-0.02, 1.02}}]
```

	1	2	3	4	5	6	7	8
Γ	A ₁	A ₁	E	E	B ₁	B ₂	A ₁	E
E(k)	0.	0.5826	0.6286	0.6286	0.8901	0.9744	1.066	1.1236
X	A ₁	B ₁	B ₂	B ₁	A ₁	A ₂	A ₁	A ₁
E(k)	0.2749	0.4424	0.6368	0.7735	0.7834	0.9446	0.9827	1.1384
M	A ₁	E	E	B ₂	E	E	B ₁	A ₁
E(k)	0.3227	0.549	0.549	0.6934	0.923	0.923	0.9836	0.9886
Γ	A ₁	A ₁	E	E	B ₁	B ₂	A ₁	E
E(k)	0.	0.5826	0.6286	0.6286	0.8901	0.9744	1.066	1.1236

Maximum Abscissa = 1.70711

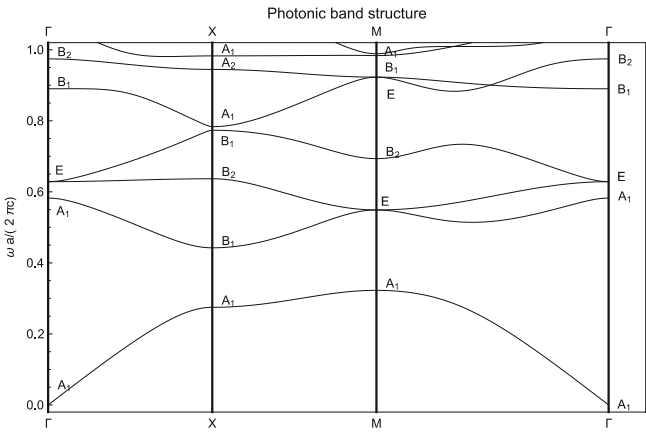


Figure 11.7 Symmetry analysis of a photonic band structure using **GTPhSymmetryBands**. The band structure refers to the example of dielectric alumina rods in air presented in Section 11.1.2.

two-fold degeneracy itself is connected with two orthogonal eigenmodes as can be seen from the images of the modes.

In Figure 11.7, the application of **GTPhSymmetryBands** is illustrated, which applies the symmetry analysis to the entire band structure. The high symmetry points of interest are specified during the band structure calculation. The output of **GTPhSymmetryBands** is presented in tabular form together with a band structure plot.

By decreasing the symmetry of a photonic crystal, degeneracies within the photonic band structure can be lifted. As an example, the band structure of rods with quadratic cross section in air is compared with rods having a rectangular cross

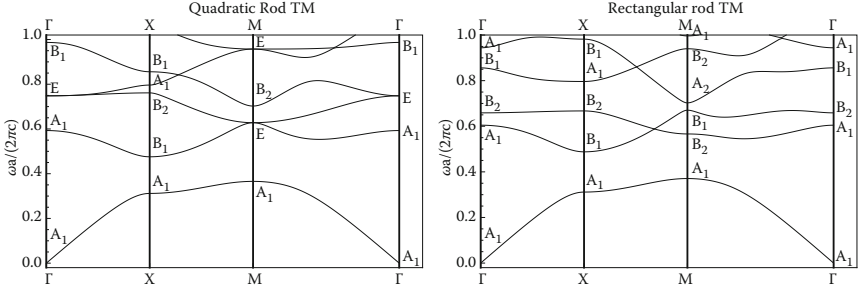


Figure 11.8 Rods ($\varepsilon = 8.9$) with quadratic and rectangular cross section in air in a square lattice. The filling factor is $\gamma = 0.08$.

section (Figure 11.8). In both cases, the filling factor is chosen to be the same, but the ratio of the side lengths is given by 2 : 1 for the rectangle. Because of this, the point group symmetry of the lattice is reduced from C_{4v} (square) to C_{2v} (rectangle). Since C_{2v} is an Abelian group, this lifts the two-fold degeneracies at the Γ and M point.

GTCompatibility can be used to demonstrate that the irreducible representation E of C_{4v} is split in the representations B_1 and B_2 of C_{2v} : $E = B_1 \oplus B_2$.

11.3

Supercells and Symmetry of Defect Modes

From the examples discussed in Sections 11.1.2 and 11.2, it can be verified that the photonic band structure of a two-dimensional photonic crystal can exhibit gaps, i.e., frequency regions with forbidden propagation of electromagnetic waves. Clearly, the photonic density of states in those frequency regions is zero.

By introducing defects to a photonic crystal, the translational symmetry is broken. Different geometries of defects can be considered, such as surfaces, lines of defects, or single localized defects as point defects. Point defects in a lattice of rods in air can be realized by a change of the permittivity or of the radius of one rod within the photonic crystal [183, 184].

By using a GREEN's function method it is possible to treat a system with one defect in an otherwise perfect photonic crystal solving a corresponding DYSON equation. Alternatively, if no GREEN's function is constructed, a supercell approach can be used, where the elementary unit cell is extended and a single defect is introduced. Since a crystal is periodic with respect to translations, the size of the supercell has to be chosen such that an interaction between two defects is negligible.

In the following, we will refer to the example of SAKODA and SHIROMA [183] and consider a square lattice of dielectric rods in air with a lattice constant of $a = 1.27$ cm, a rod radius of $r = 0.48$ cm $= 0.378a$, and a permittivity of $\varepsilon = 9.0$. For the present discussion, the band structure was calculated using MPB. GTPack is used to plot the band structure and to calculate the density of states (cf. Figure 11.9). Within the spectrum three gaps can be found.

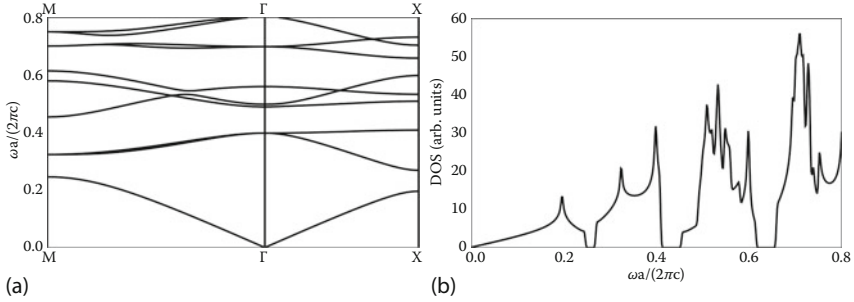


Figure 11.9 Photonic bands and density of states of the ideal structure (square lattice with rods in air, TM-polarization, $\epsilon = 9.0$, $r = 0.378a$). (a) Band structure; (b) density of states.

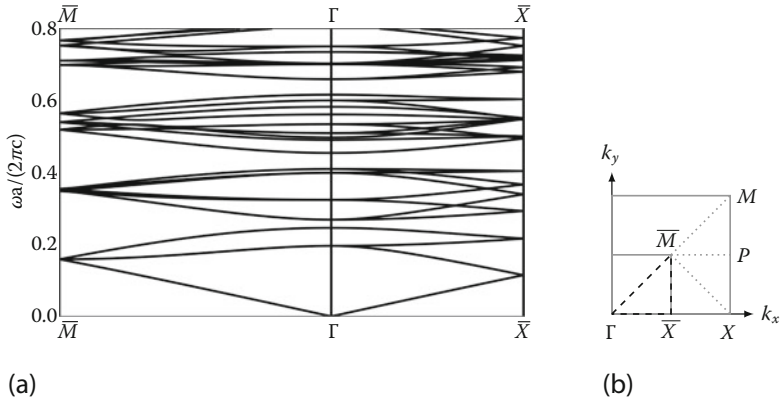


Figure 11.10 Band structure of the perfect structure calculated using a 2×2 supercell. (a) Band structure of the 2×2 supercell. (b) Quarter of the BRILLOUIN zone of the primitive cell and the supercell.

At first, the effect of constructing a supercell on the band structure is studied. By constructing a 2×2 supercell (2 primitive cells in each direction) the unit cell becomes four times as large as the primitive cell. Thus, the size of the BRILLOUIN zone of the supercell reduces to a quarter of the size of the original BRILLOUIN zone. Comparing the band structure of the supercell plotted in Figure 11.10a with the original band structure in Figure 11.9, it can be verified that bands are folded into the smaller BZ of the supercell. This effect becomes clear if only the lowest band is considered.

Figure 11.10b demonstrates how the symmetry points and lines in reciprocal space of the primitive cell are transferred to the supercell BZ symmetry points by reciprocal lattice vectors of the supercell. Particularly parts of the symmetry lines $\Gamma - X$, $\Gamma - M$, and $M - X$ are folded back to the small cell as:⁴⁾ $\bar{X} - X \rightarrow \bar{X} - \Gamma$, $X - P \rightarrow \Gamma - \bar{X}$, $P - M \rightarrow \bar{X} - \Gamma$, $\bar{M} - M \rightarrow \bar{M} - \Gamma$, $X - \bar{M} \rightarrow \Gamma - \bar{M}$. From Figure 11.11 it can be verified how the two band structures are related. The density of states is

4) P is used to distinguish the symmetry points. In terms of the supercell it is a point $\bar{X}$.

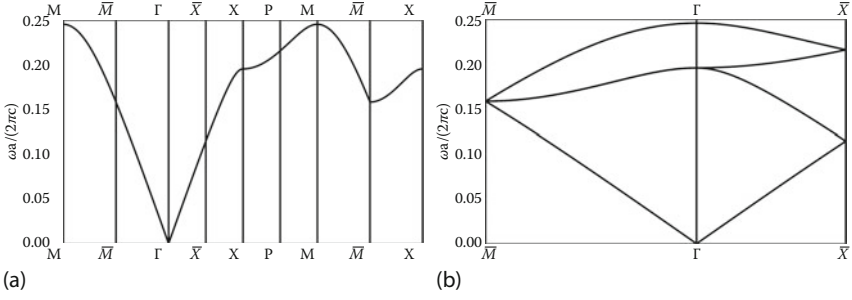


Figure 11.11 Folding of the first band of Figure 11.10a into the smaller BZ of the 2×2 supercell. (a) Band calculated with respect to the folding procedure. (b) Band folded into the smaller BZ of the supercell.

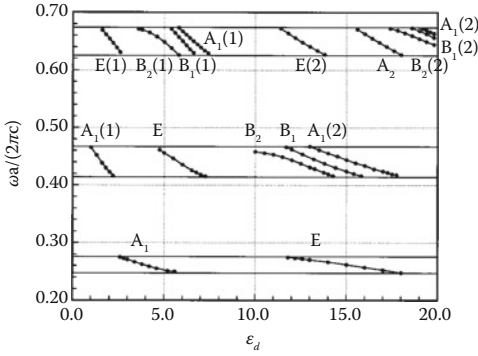


Figure 11.12 Eigenfrequencies of the localized defect modes in the three gaps of the TM band structure as a function of the permittivity ϵ_d of the defect rod. Numbers in brackets behind the names of the irreducible representations denote the multiplicity. The picture is taken from [183]. (With permission, Copyright © 1997, American Physical Society.)

independent of the choice of the unit cell. Therefore it is advantageous to compare the density of states if very large supercells are constructed, as the back folding of the photonic bands becomes tedious in this case.

In the work of SAKODA and SHIROMA [183], defects are generated by changing the permittivity of a single rod in the range of $1 \leq \epsilon_d \leq 20$. The limit $\epsilon_d = 1$ represents a removal of the dielectric rod or a vacancy. The supercell size is chosen to be 12×12 . Figure 11.12 shows which defect states occur within the three gaps found within the density of states of the pure photonic crystal.

Example 58 (Symmetry classification of defect modes). Using MPB a setup similar to [183] was constructed using a 11×11 supercell. Defect modes were calculated for a permittivity of $\epsilon_d = 15$. The calculated fields are imported using **GTPhMPBFields** as shown in Figure 11.13. The point group of the lattice is given by C_{4v} . The symmetry of the defects can be analyzed by means of **GTPack** using **GTPhSymmetryField**. The analysis is performed in the first and the second gap within the photonic spectrum. In agreement with Figure 11.12, the defect states in the first gap belong to the two-dimensional irreducible representation E and the defect states in the second gap belong to the two one-dimensional irreducible representations A_1 and B_1 .

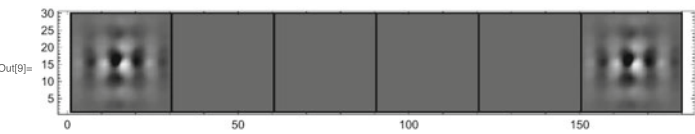
Mathematica
GTPhMPBFields, GTPhSymmetryField

The character table of the point group C_{4v} is calculated and stored in `c4vct`. The defect modes resulting from MPB calculations are read and analysed with respect to their symmetry.

Gap 1

```
In[8]:= gap1 = GTPhMPBFields["gap1.h5", {"Bloch wavevector", "z.r-new", "z.i-new"},  
    GOTransformation -> True];  
  
In[9]:= GTPhSymmetryField[gap1[[2]], c4vct, 30, GOPlot -> True,  
    GOPlotStyle -> "Im", ColorFunction -> "GrayTones"]
```

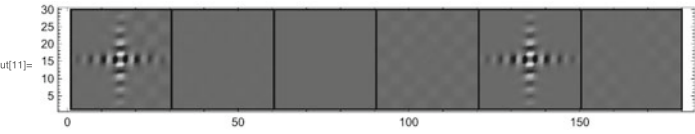
	A ₁	A ₂	B ₂	B ₁	E
Norm	0.000188268	6.90115×10^{-9}	2.47255×10^{-8}	1.01782×10^{-8}	99.9998



Gap 2

```
In[10]:= gap21 = GTPhMPBFields["gap2_1.h5", {"Bloch wavevector", "z.r-new", "z.i-new"},  
    GOTransformation -> True];  
  
In[11]:= GTPhSymmetryField[gap21[[2]], c4vct, 30,  
    GOPlot -> True, GOPlotStyle -> "Im", ColorFunction -> "GrayTones"]
```

	A ₁	A ₂	B ₂	B ₁	E
Norm	0.0146683	0.00016862	0.466652	99.0867	0.431767



```
In[12]:= gap22 = GTPhMPBFields["gap2_2.h5", {"Bloch wavevector", "z.r-new", "z.i-new"},  
    GOTransformation -> True];  
  
In[13]:= GTPhSymmetryField[gap22[[2]], c4vct, 30,  
    GOPlot -> True, GOPlotStyle -> "Im", ColorFunction -> "GrayTones"]
```

	A ₁	A ₂	B ₂	B ₁	E
Norm	99.9485	0.0000314957	0.0327229	0.0000515577	0.018701

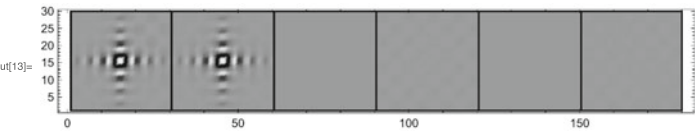


Figure 11.13 Determination of the symmetry of the defect modes for $\epsilon_d = 15$ in the first and second gap using `GTPhMPBFields` and `GTPhSymmetryField`. The result agrees with the symmetry classification given in Figure 11.12.

11.4

Uncoupled Bands

Uncoupled bands	
GTPhUncoupledBands	Discards uncoupled bands from a photonic band structure

Photonic band structures and defect modes in photonic spectral gaps were addressed by examples in Sections 11.1– 11.3. A photonic gap means that photons cannot propagate in the sample within a certain frequency range. Experimentally, photonic band structures can be verified by means of transmission experiments. However, in comparison to theoretical predictions, systematic differences between experiments and theory were observed and reported [185–187]. These differences can be explained via so-called “uncoupled bands”, which cannot be excited by incident plane waves. Because of uncoupled bands the measured transmission spectrum does not reflect the theoretical photonic density of states. In the following, uncoupled bands are discussed in the context of symmetry arguments [29, 188].

As before, the square lattice of dielectric rods in air serves as a good example. An external incident plane wave with polarization in the z -direction is considered. Inside the crystal the wave shall propagate in the x -direction ($\mathbf{k} = k_0 \mathbf{e}_x$). The z -component of the electric field of the plane wave is given by (amplitude factors do not play a role)

$$E_z(\mathbf{r}, t) = e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} = e^{i(k_0 x - \omega t)}. \quad (11.6)$$

Since there is no dependence of the field on the y -coordinate, the x - z -plane forms a mirror plane. Hence, the group of the wave vector $\mathcal{G}_0(\mathbf{k})$ is C_s for the Γ - X direction within the BRILLOUIN zone of the square lattice. Furthermore, the plane wave (11.6) is a basis function of the identity representation A' as demonstrated in Figure 11.14 by using **GTCharProjectionOperator**. Basis functions of the A'' representation have to be odd functions with respect to y , e.g., $\sin(k_y y)$.

To figure out, which bands are uncoupled bands, i.e., not coupling to the incident plane wave, the compatibility relations of bands have to be taken into account (**GTCompatibility**). In the present case, the group of the wave vector $\mathcal{G}_0(\mathbf{k})$ is given by C_{2v} at the X point and by C_{4v} at Γ . The compatibility relations allow one to find the symmetry of the lowest bands algebraically by starting from Figure 11.2. The lowest two bands have A_1 symmetry at Γ and, thus, it follows from the compatibility that they also keep the symmetry of the totally symmetric representation along Γ - X (A'). Since $C_s \subset C_{4v}$ and since C_s is Abelian, the two-dimensional representation E at Γ splits along Γ - X . According to Figure 11.15, the irreducible representations E and B_2 are compatible only via a band having the A'' representation. Thus, the third band along the line Γ - X is an uncoupled band and won't be observed in an experiment using the plane-wave from (11.6).

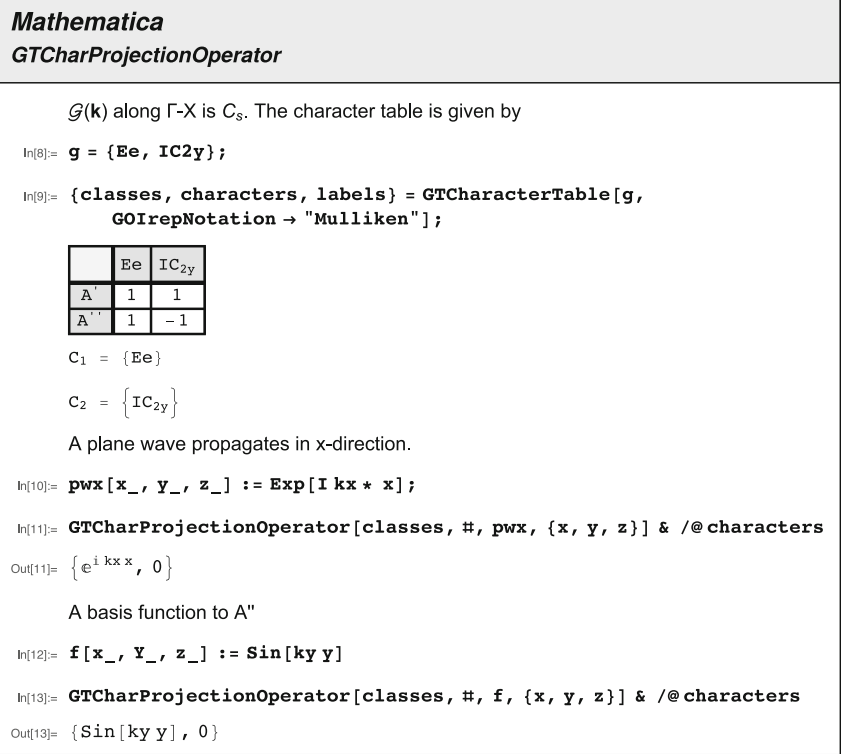


Figure 11.14 Basis functions of the irreducible representations of C_{4v} in terms of external plane waves.

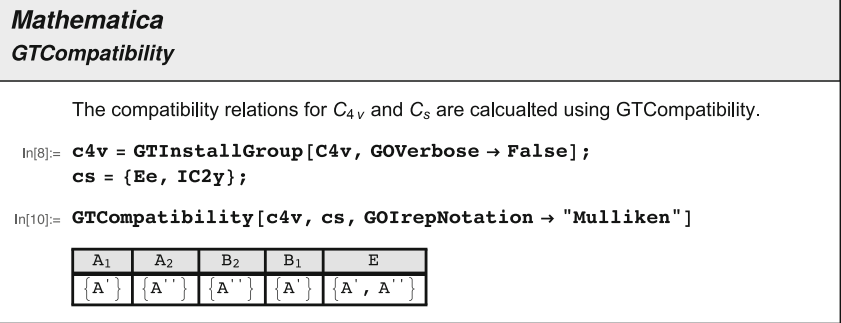


Figure 11.15 Calculating the compatibility relation between C_{4v} and $C_s \subset C_{4v}$ using GTCompatibility.

Alternatively, the study of uncoupled bands is possible by analysis of the symmetry of the eigenvectors calculated in connection to the photonic band structure. The eigenmode follows from the coefficients $c_\nu(\mathbf{k})$ of the ν th band at the point $\mathbf{k}$

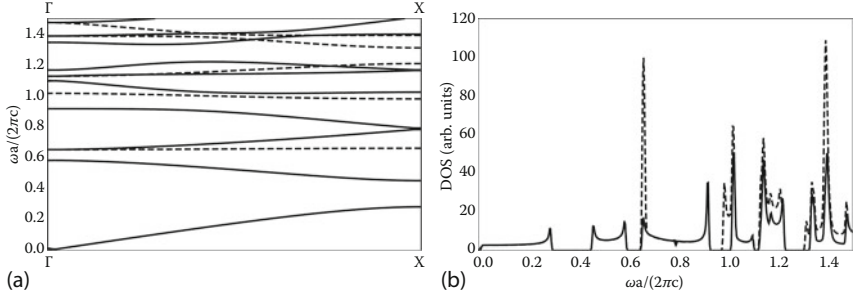


Figure 11.16 Uncoupled bands in the square lattice (a) Band structure along Γ –X (dashed line: uncoupled bands); (b) full DOS along Γ –X (dashed line) and DOS without uncoupled bands (solid lines).

in the BRILLOUIN zone as

$$E_{\nu,\mathbf{k}}^z(\mathbf{r}) = \sum_{\mathbf{G}} c_{\nu}(\mathbf{k}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}. \quad (11.7)$$

Character projection operators can be used to figure out if (11.7) is a basis function of an irreducible representation of the corresponding group of the wave vector.⁵⁾ In some cases it suffices to observe if the eigenmode is symmetric or antisymmetric with respect to a certain symmetry operation (like a mirror plane). Within GTPack, the command **GTPhUncoupledBands** can be used to find uncoupled bands within a photonic band structure. A plot for the square lattice of dielectric rods in air along the path Γ –X is shown in Figure 11.16a. The result agrees with the outcome of the compatibility relations.

A third way to illustrate uncoupled bands is given by investigating the density of states and restricting the calculation to states along Γ –X. Since the problem effectively becomes one-dimensional, the typical VAN HOVE singularities can be observed (Figure 11.16b). The first uncoupled band within the photonic band structure is very flat. Therefore, it contributes with a large peak at the upper end of the second gap within the full density of states. As soon as the uncoupled band is removed, the density of states decreases drastically in this frequency range. Within the third gap, removing the contribution of the uncoupled band to the density of states causes an increase of the photonic band gap.

Task 40 (Uncoupled bands). Identify the uncoupled bands for the square lattice of dielectric rods in air ($\varepsilon = 8.9$, $r = 0.2a$) for an incident plane wave propagating in Γ –M direction.

- Start from the irreducible representations at the Γ and M point of the BRILLOUIN zone and use the compatibility relations.
- Find the uncoupled bands using **GTPhUncoupledBands** or use the character projection operator explicitly.

5) As demonstrated in Section 11.2, the analysis might be based on MPB calculations as well.

12

Three-Dimensional Photonic Crystals

Symmetrie, ob man ihre Bedeutung weit oder eng fasst, ist eine Idee, vermöge derer der Mensch durch die Jahrtausende seiner Geschichte versucht hat Ordnung, Schönheit und Vollkommenheit zu begreifen und zu schaffen.

*H. Weil and L. Bechtolsheim
(Symmetrie, Birkhäuser 1981)*

Throughout the chapter the calculation of photonic band structures for three-dimensional photonic crystals is discussed. In contrast to two-dimensional photonic crystals, the two linear independent polarizations cannot be handled separately. The vector fields transform as basis functions of the irreducible representations of the group of the master equation at specific $\mathbf{k}$ points within the BRILLOUIN zone. Therefore, irreducible representations can be assigned in a similar way as discussed for electronic energy bands or two-dimensional photonic crystals. An example will be given, by means of three-dimensional dielectric spheres in a cubic lattice. The solution of the master equation may be also considered as a multiple scattering problem. In such a formalism vector spherical harmonics serve as basis functions. The chapter closes by a discussion of properties of vector spherical harmonics.

12.1

Empty Lattice Bands and Compatibility Relations

The ansatz for the vector field $\mathbf{H}(\mathbf{r})$ in the master equation (10.14) is given by

$$\mathbf{H}(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{G}, \lambda} h_{\mathbf{G}}^{\lambda}(\mathbf{k}) \mathbf{e}_{\mathbf{G}}^{\lambda} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}}. \quad (12.1)$$

The two independent polarizations $\mathbf{e}_{\mathbf{G}}^1, \mathbf{e}_{\mathbf{G}}^2$ have to be such that $(\mathbf{k} + \mathbf{G})$, $\mathbf{e}_{\mathbf{G}}^1$, and $\mathbf{e}_{\mathbf{G}}^2$ are mutually orthogonal, corresponding to the transversal nature of the elec-

tromagnetic field. The polarization vectors are defined as

$$\mathbf{e}_G^1 = \frac{\mathbf{c} \times (\mathbf{k} + \mathbf{G})}{|\mathbf{c} \times (\mathbf{k} + \mathbf{G})|}, \quad \mathbf{e}_G^2 = \frac{\mathbf{e}_G^1 \times (\mathbf{k} + \mathbf{G})}{|\mathbf{e}_G^1 \times (\mathbf{k} + \mathbf{G})|}, \quad (12.2)$$

where $\mathbf{c}$ is an arbitrary vector.¹⁾

In the following, the empty lattice photonic band structure is discussed for the example of a simple cubic lattice. Since the solutions of the master equation are basis functions of the irreducible representations of the underlying symmetry group, the character projection operator can be applied to determine which component of (12.1) belongs to which irreducible representation. The GTPack command **GTCharProjectionOperator** is capable of handling vector-valued functions, as shown in Figure 12.1. The group $\mathcal{G}_0(\mathbf{k})$ at the X point of the BRILLOUIN zone of a simple cubic lattice is given by the point group D_{4h} . For an empty lattice calculation, the lowest eigenmode is connected to the reciprocal lattice vector $\mathbf{G} = (0, 0, 0)2\pi/a$. The two transversal modes are²⁾

$$\mathbf{H}_1(\mathbf{r}) = e^{i\pi z} \mathbf{e}_x, \quad \mathbf{H}_2(\mathbf{r}) = e^{i\pi z} \mathbf{e}_y. \quad (12.3)$$

Applying the character projection operator to $\mathbf{H}_1$ and $\mathbf{H}_2$ it can be seen that the fields contain parts transforming like the first and second rows of T_{1u} and T_{2u} , respectively. A special case occurs for the lowest eigenmode at Γ ($\mathcal{G}_0(\mathbf{k}) = O_h$). Because of $\mathbf{k} = \mathbf{G} = (0, 0, 0)2\pi/a$, the difference between transversal and longitudinal vector fields vanishes, leading to constant fields with three linear independent directions. This mode belongs to the representation T_{1u} .

Alternatively, to obtain the irreducible representations associated with the empty lattice bands, it is possible to construct reducible representations and decompose them in terms of a CLEBSCH–GORDAN sum with respect to the irreducible representations of the corresponding group $\mathcal{G}_0(\mathbf{k})$. As explained in Example 56, this method is implemented within the command **GTPwEmptyLatticeRep**³⁾.

Within the algorithm a set of reciprocal lattice vectors is generated using **GTLatCluster**. The vectors $\mathbf{k} + \mathbf{G}$ to a certain $\mathbf{k}$ vector are ordered in shells with respect to their norm (**GTLatShells**). All vectors of a shell finally lead to the same eigenmode frequency in the empty lattice band structure. At the X point in the BRILLOUIN zone of the simple cubic lattice ($\mathcal{G}_0(\mathbf{k}) = D_{4h}$) the first shell ($\mathbf{G} = (0, 0, 0)2\pi/a$) contains the two vectors $\mathbf{k}_1 = (0, 0, 1/2)2\pi/a$ and $\mathbf{k}_2 = (0, 0, -1/2)2\pi/a$, where $\mathbf{k}_2$ differs from $\mathbf{k}_1$ by a reciprocal lattice vector. In the next step, the number of totally invariant vectors under the individual operations of the group have to be determined. The point group D_{4h} contains 16 operations and 10 classes. The vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ are invariant under transformations belonging to operations of the classes $\{E\}$, $\{C_{4z}, C_{4z}^{-1}\}$, $\{C_{2z}\}$, $\{IC_{2x}, IC_{2y}\}$, and $\{IC_{2a}, IC_{2b}\}$ since they point along the rotation axis or lie in the mirror planes. Thus, the polarizations $\mathbf{e}_1$ and

1) In contrast to (10.35) and (10.36) the vector $\mathbf{c}$ is used instead of $\mathbf{e}_z$. This helps to avoid numerical instabilities during calculations.

2) $\mathbf{c} = (1, 0, 0)$ used in (12.2).

3) Details can be found in [27].

Mathematica

Consider the X-point with $\mathbf{G}=(0,0,0)$. Polarisations $\mathbf{e}_1$ and $\mathbf{e}_2$ perpendicular to $(\mathbf{k}+\mathbf{G})$ are considered. cld4h and chard4h contain the classes and characters of D_{4h} .

```

In[8]:= k = {0, 0, 1/2}; c = {0, 1, 0}; e1 = Cross[c, k];
e1 = e1 / Norm[e1];
e2 = Cross[e1, k];
e2 = e2 / Norm[e2];

In[10]:= e1 = {1, 0, 0}; e2 = {0, 1, 0};

Construct two plane waves.

In[11]:= f1[x_, y_, z_] := e1 * Exp[I 2 π k. {x, y, z}];
f2[x_, y_, z_] := e2 * Exp[I 2 π k. {x, y, z}];

In[12]:= symm = Select[Transpose[{names,
  GTCharProjectionOperator[cld4h, chard4h, f1, {x, y, z}] // FullSimplify,
  GTCharProjectionOperator[cld4h, chard4h, f2, {x, y, z}] // FullSimplify}],
  #[[2]] != {0, 0, 0} &];
Grid[Prepend[symm, {" ", "f1", "f2"}] // Transpose, Frame → All,
  Background →
    {{GTBackGroundColor1}, {GTBackGroundColor1}, {1, 1} → GTCornerColor}]

```

Out[13]=

	T_{1u}	T_{2u}
f1	$\{\cos[\pi z], 0, 0\}$	$\{i \sin[\pi z], 0, 0\}$
f2	$\{0, \cos[\pi z], 0\}$	$\{0, i \sin[\pi z], 0\}$

Consider the lowest eigenmode at the Γ -point ($\mathbf{k}=(0,0,0)$, $\mathbf{G}=(0,0,0)$). No distinction appears between transversal and longitudinal components. cloh and charoh contain classes and characters of O_h .

```

In[14]:= f0[x_, y_, z_] := {1, 0, 0}; f1[x_, y_, z_] := {0, 1, 0}; f2[x_, y_, z_] := {0, 0, 1}

In[15]:= symm = Select[Transpose[
  {names, GTCharProjectionOperator[cloh, charoh, f0, {x, y, z}] // FullSimplify,
  GTCharProjectionOperator[cloh, charoh, f1, {x, y, z}] // FullSimplify,
  GTCharProjectionOperator[cloh, charoh, f2, {x, y, z}] // FullSimplify}],
  #[[2]] != {0, 0, 0} &];
Grid[symm // Transpose, Frame → All, Background → {None, {GTBackGroundColor1}}]

```

Out[16]=

T_{1u}
$\{1, 0, 0\}$
$\{0, 1, 0\}$
$\{0, 0, 1\}$

Figure 12.1 Symmetrized plane waves at the X and Γ point of the BRILLOUIN zone for a simple cubic lattice. Only such irreducible representations are selected where the projection gives nonzero results.

$\mathbf{e}_2$ are orthogonal vectors in a plane perpendicular to the corresponding $\mathbf{k}$,

$$\mathbf{H}_1 = \mathbf{e}_1 e^{i\mathbf{k} \cdot \mathbf{r}}, \quad \mathbf{H}_2 = \mathbf{e}_2 e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (12.4)$$

If a rotation of the set leaving the two $\mathbf{k}$ vectors invariant (rotation angle θ) is applied, the vector fields transform like⁴⁾

$$\underline{\underline{R}}_{\theta}(T) \begin{pmatrix} \mathbf{H}_1 \\ \mathbf{H}_2 \end{pmatrix} = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} \mathbf{H}_1 \\ \mathbf{H}_2 \end{pmatrix}. \quad (12.5)$$

4) $\underline{\underline{R}}_{\theta}$ represents the transformation matrix of a rotation about an angle θ and $\underline{\underline{R}}_i$ is the corresponding matrix of a mirror operation.

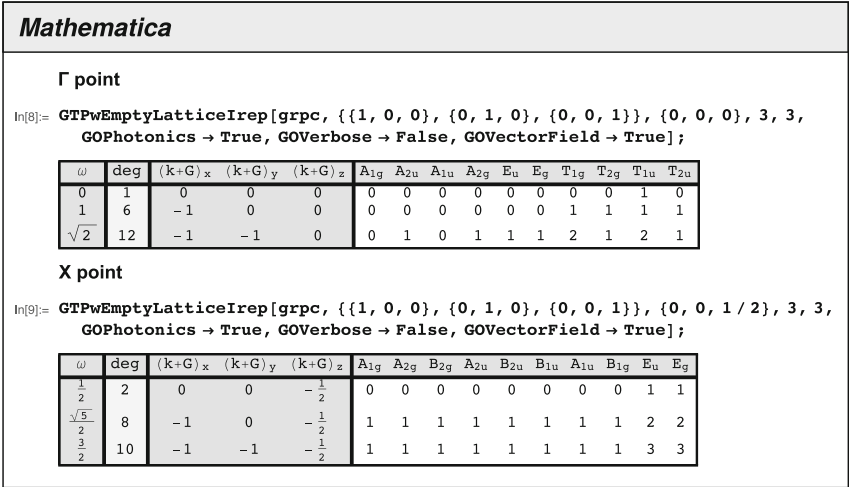


Figure 12.2 Irreducible representations at the Γ and X point of the BRILLOUIN zone of the simple cubic lattice (empty lattice test).

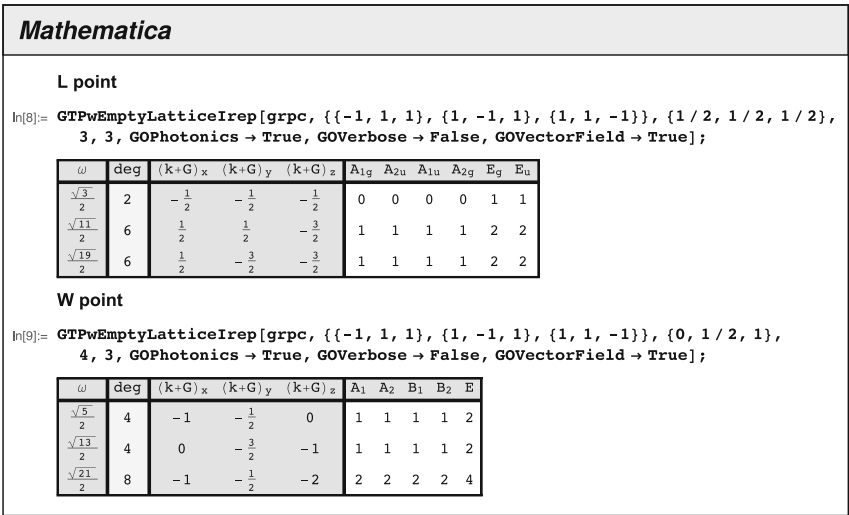


Figure 12.3 Irreducible representations at the L and W point of the BRILLOUIN zone of the face-centered cubic lattice (empty lattice test).

The transformation matrix is considered as a representation matrix with character $\chi_\theta(T) = 2 \cos \theta$. For a similar discussion of a mirror operation one of the vectors $\mathbf{e}_i$ is considered to be in the mirror plane and to remain unchanged under the transformation. The second vector, however, is perpendicular to the mirror

Mathematica

oh, c4v, d4h contain the groups O_h , C_{4v} , D_{4h} respectively.

Compatibility $\Gamma - \Delta$

In[8]:= **GTCompatibility**[oh, c4v, GOIrepNotation → "Mulliken"]

A _{1g}	A _{2u}	A _{1u}	A _{2g}	E _u	E _g	T _{1g}	T _{2g}	T _{1u}	T _{2u}
{A ₁ }	{B ₂ }	{A ₂ }	{B ₁ }	{A ₂ , B ₂ }	{A ₁ , B ₁ }	{A ₂ , E}	{B ₂ , E}	{A ₁ , E}	{B ₁ , E}

Compatibility X - Δ

In[9]:= **GTCompatibility**[d4h, c4v, GOIrepNotation → "Mulliken"]

A _{1g}	A _{2g}	B _{2g}	A _{2u}	B _{2u}	B _{1u}	A _{1u}	B _{1g}	E _u	E _g
{A ₁ }	{A ₂ }	{B ₂ }	{A ₁ }	{B ₁ }	{B ₂ }	{A ₂ }	{B ₁ }	{E}	{E}

Figure 12.4 Compatibility relations between the irreducible representations along $\Gamma - \Delta - X$ for the simple cubic and face-centered cubic structure.

plane and changes sign,

$$\underline{\underline{R}}_f(T) \begin{pmatrix} \mathbf{H}_1 \\ \mathbf{H}_2 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \mathbf{H}_1 \\ \mathbf{H}_2 \end{pmatrix}. \quad (12.6)$$

The resulting character is $\chi_f(T) = 0$. Those characters multiplied by the number of invariant vectors, calculated in the first step, defines the characters of a faithful representation of $\mathcal{G}_0(\mathbf{k})$. The decomposition into irreducible representations is based on Theorem 21 equation (5.38). Figures 12.2 and 12.3 demonstrate the method. The option **GOVectorFields** of the command **GTPwEmptyLattice** forces the command to apply the transformation rules for vector fields. The frequency is given in units of $\omega a / (2\pi c)$. The degeneracy of the mode, as well as a characteristic vector $\mathbf{k} + \mathbf{G}$ are presented besides the decomposition in terms of irreducible representations.

The compatibility relations in Figure 12.4, given exemplarily for the line $\Gamma - \Delta - X$, can be used to check the results of the symmetry analysis in the next section.

12.2

An example: Dielectric Spheres in Air

As an example of a photonic band structure calculation for a three-dimensional photonic crystal, a system of dielectric spheres in air arranged in a simple cubic lattice is considered [27, 190]. The spheres are defined to have a radius of $0.3a$, a denotes the lattice constant, and a permittivity of $\varepsilon = 13$. The photonic band structures will be calculated by using GTPack and MPB. Within the group theoretical analysis the eigenmodes calculated with MPB are used.

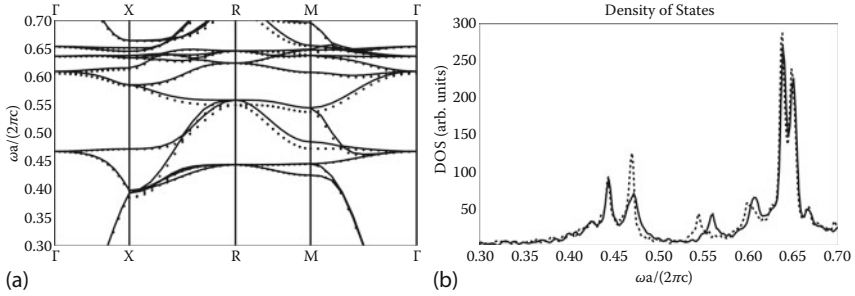


Figure 12.5 Band structure and density of states for dielectric spheres in air in a simple cubic lattice ($\epsilon = 13, r = 0.3a$), dotted line: GTPack using the matrix inversion method for $\kappa(\mathbf{G}, \mathbf{G}')$, solid line: MPB calculation. (a) Photonic band structure; (b) density of states.

The calculated photonic band structure and the density of states is plotted in Figure 12.5. Within photonic band structure calculations, numerical deviations may arise depending on how the calculation of $\kappa(\mathbf{G})$ denoting the FOURIER transform of $1/\epsilon(\mathbf{r})$ is performed⁵⁾. Instead of calculating the FOURIER transform of $1/\epsilon(\mathbf{r})$ directly it is advantageous to calculate the matrix $\epsilon(\mathbf{G}, \mathbf{G}')$ (which is the FOURIER transform of $\epsilon(\mathbf{r})$) first and to calculate the inverse matrix afterwards. This approach was initially described by Ho *et al.* [191] and is also implemented in GTPack. In the asymptotic limit (large number of $\mathbf{G}$ vectors) both methods lead to identical results. Values for $\kappa(\mathbf{G})$ calculated prior to the band structure calculations can be used with **GTPhBandsObjects**. For the GTPack calculation plotted in Figure 12.5 1419 plane waves are used.

The symmetry analysis is based on similar ideas to those discussed in Section 11.2, with the difference of taking into account the vector nature of the eigenmodes. Whereas in the two-dimensional case, a splitting of the problem into two separate problems (with respect to the two linearly independent polarizations) characterized by scalar fields is possible, such a decomposition does not apply to the three-dimensional case. However, as shown in Figure 12.1 the application of the character projection operator implemented in **GTCharProjectionOperator** also works for vector fields. Thus, the extension of the symmetry analysis using **GTPhSymmetryAnalysis** to the three-dimensional case is straightforward.

Figure 12.6 shows the result of the analysis achieved by applying **GTPhSymmetryAnalysis** to the example of dielectric spheres in air arranged in a simple cubic lattice. Since multiple modes are close to each other in the frequency range, an automatic labeling given by **GTPhSymmetryAnalysis** might appear confusing (see Figure 12.6a). Improvements can be achieved by applying **GTBandsPlotImprove** as shown in Figure 12.6b. Additionally, the interactive drawing tools of *Mathematica* can be used. The symmetry analysis presented in Figure 12.6b is in agreement with [27, 190].

5) Slight deviations can be found by comparing the calculated MPB band structure with the result published by SAKODA [27, 190].

scattering theory [188, 192–196]. In electronic structure theory, a similar method is given by the KORRINGA–KOHN–ROSTOKER (KKR) method [197, 198]. If a photonic crystal consists of spheres arranged in a lattice, the multiple-scattering process can be obtained in terms of multiple single-site scattering events, where the scattering of light at each sphere is described by the classical MIE scattering problem [199–201]. The major difference to the scattering problem in electronic structure theory is that due to the vector nature of the fields in the photonic case, two independent polarizations have to be considered, leading to two scattering t -matrices instead of one. Whereas an expansion in spherical harmonics is used in electronic structure theory, vector spherical harmonics appear in the photonic scattering theory.

For a linear, isotropic and homogeneous medium, the electric and magnetic fields must satisfy the following vector wave equations (time dependence separated, see Section 10.1),

$$\nabla^2 \mathbf{E}(\mathbf{r}) + k^2 \mathbf{E}(\mathbf{r}) = 0, \quad \nabla^2 \mathbf{H}(\mathbf{r}) + k^2 \mathbf{H}(\mathbf{r}) = 0, \quad (12.7)$$

where $k^2 = \omega^2 \varepsilon_0 \varepsilon_r \mu_0 \mu_r = (\omega/c)^2 \varepsilon_r \mu_r$. Furthermore, the fields are divergence-free, meaning

$$\nabla \cdot \mathbf{E}(\mathbf{r}) = 0, \quad \nabla \cdot \mathbf{H}(\mathbf{r}) = 0. \quad (12.8)$$

Theorem 46 (Vector wave functions). *Given a scalar function $\psi(\mathbf{r})$ and an arbitrary constant vector $\mathbf{c}$ then the vector function*

$$\mathbf{M}(\mathbf{r}) = \nabla \times (\mathbf{c}\psi(\mathbf{r})) = -\mathbf{c} \times \nabla \psi(\mathbf{r}) \quad (12.9)$$

is divergence-free and a solution of a vector wave equation (12.7) if $\psi(\mathbf{r})$ is a solution of the scalar wave equation

$$\nabla^2 \psi(\mathbf{r}) + k^2 \psi(\mathbf{r}) = 0. \quad (12.10)$$

Furthermore, the vector function

$$\mathbf{N}(\mathbf{r}) = \frac{1}{k} \nabla \times \mathbf{M}(\mathbf{r}), \quad (12.11)$$

represents another solution of equations (12.7). If $\mathbf{c} = \mathbf{r}$ is used ($\mathbf{r}$ – radius vector), then $\mathbf{M}(\mathbf{r})$ and $\mathbf{N}(\mathbf{r})$ represent the solutions of the vector wave equation (12.7) formulated in spherical coordinates.

Task 41 (Vector wave functions). *Proof Theorem 46!*

The scalar wave equation (12.10) formulated in spherical coordinates can be solved by separating the function $\psi(\mathbf{r})$ into a radial part $R(r)$ and an angular part $\Phi(\theta, \varphi)$ according to

$$\psi(\mathbf{r}) = R(r)\Phi(\theta, \varphi). \quad (12.12)$$

Table 12.1 Transformation of vector operators under proper $T_R^p \hat{=} \underline{\mathbb{R}}$ and improper $T_R^i \hat{=} \underline{\mathbb{R}}$ rotations.

Proper rotation	Improper rotation
$\hat{P}(T_R^p) \hat{\mathbf{P}} \hat{P}((T_R^p)^{-1}) = \hat{\mathbf{P}}$	$\hat{P}(T_R^i) \hat{\mathbf{P}} \hat{P}((T_R^i)^{-1}) = \hat{\mathbf{P}}$
$\hat{P}(T_R^p) \hat{\mathbf{L}} \hat{P}((T_R^p)^{-1}) = \hat{\mathbf{L}}$	$\hat{P}(T_R^i) \hat{\mathbf{L}} \hat{P}((T_R^i)^{-1}) = -\hat{\mathbf{L}}$
$\hat{P}(T_R^p) (\hat{\mathbf{P}} \times \hat{\mathbf{L}}) \hat{P}((T_R^p)^{-1}) = (\hat{\mathbf{P}} \times \hat{\mathbf{L}})$	$\hat{P}(T_R^i) (\hat{\mathbf{P}} \times \hat{\mathbf{L}}) \hat{P}((T_R^i)^{-1}) = (\hat{\mathbf{P}} \times \hat{\mathbf{L}})$

The solutions of the corresponding differential equations for the angular part are spherical harmonics $Y_{l,m}(\theta, \varphi)$, whereas the solutions of the radial equation are the spherical BESSEL functions $j_l(kr)$ or NEUMANN functions $n_l(kr)$ ⁶⁾ Analogously, the solution of the vectorial scattering problem can be formulated as a series expansion in terms of vector spherical waves. Following Theorem 46, the vector spherical waves for the electrical field are defined as⁷⁾

$$\begin{aligned} \mathbf{E}_L^M(\mathbf{r}) &= \hat{\mathbf{P}}^M j_l(kr) Y_{l,m}(\theta, \varphi) & \hat{\mathbf{P}}^M &= i\hat{\mathbf{L}} = \mathbf{r} \times \nabla, \\ \mathbf{E}_L^N(\mathbf{r}) &= \hat{\mathbf{P}}^N j_l(kr) Y_{l,m}(\theta, \varphi) & \hat{\mathbf{P}}^N &= \frac{i}{k} \nabla \times \hat{\mathbf{L}}, \end{aligned} \quad (12.13)$$

where $\hat{\mathbf{L}} = -i\mathbf{r} \times \nabla$ is the angular momentum operator. The rotation of scalar and vector fields was discussed in Section 2.2. If the rotation is represented by a matrix $\underline{\mathbb{R}}$ then the transformations are given by

$$\tilde{\psi}(\mathbf{r}) = \psi(\underline{\mathbb{R}}^{-1}\mathbf{r}), \quad \tilde{\mathbf{E}}(\mathbf{r}) = \underline{\mathbb{R}} \mathbf{E}(\underline{\mathbb{R}}^{-1}\mathbf{r}). \quad (12.14)$$

Analogously to the discussion of the group of the master equation in Section 10.2, Theorem 45, the transformation behavior of vector operators can be discussed. Vector fields are generated by vector operators $\hat{\mathbf{V}}$ operating on scalar fields $\psi(\mathbf{r})$. If T_R^p is a proper rotation then the rotation itself commutes with $\hat{\mathbf{V}}$. For an improper rotation T_R^i a sign change occurs. The transformation behavior for the operators $\hat{\mathbf{P}}$, $\hat{\mathbf{L}}$, and $(\hat{\mathbf{P}} \times \hat{\mathbf{L}})$ is summarized in Table 12.1 (see also OHTAKA and TANABE [194]).

According to definition (12.13) and Table 12.1 symmetry considerations are simplified, since they are related to the symmetry properties of the scalar field $j_l(kr)Y_{l,m}(\theta, \varphi)$. A rotation of the field does not effect the spherical BESSEL function in (12.13). Symmetrized vector spherical waves can be constructed as follows.

6) Alternatively, linear combinations of spherical harmonics like tesseral spherical harmonics (see Section A.2) or spherical HANKEL functions as linear combinations of the corresponding BESSEL and NEUMANN functions can be used.

7) L is a combined index $L = \{l, m\}$.

- 1. Use projection operators to generate symmetrized spherical harmonics that transform corresponding to an irreducible representation of the point group $\mathcal{G}_0$ of the system.
- 2. Multiply the spherical harmonics part by the spherical BESSEL function to obtain an expression for the scalar field.
- 3. Construct the vector-spherical wave by operating with $\hat{\mathbf{P}}^M, \hat{\mathbf{P}}^N$ on the symmetry-adapted scalar field. For the calculation of M-waves, a sign change has to be taken into account for improper symmetry elements.

Example 59 (Symmetry-adapted tesseral harmonics for C_{4v}). Tesseral harmonics represent special linear combinations of complex spherical harmonics leading to real-valued functions (see Appendix A). The construction of symmetry-adapted basis functions for a list of given functions according to irreducible representations of a certain point group can be performed automatically using **GTSymmetryBasisFunctions** as shown in Figure 12.7. Each of the tesseral harmonics S_l^m represents a basis function to one of the irreducible representations of C_{4v} . For ex-

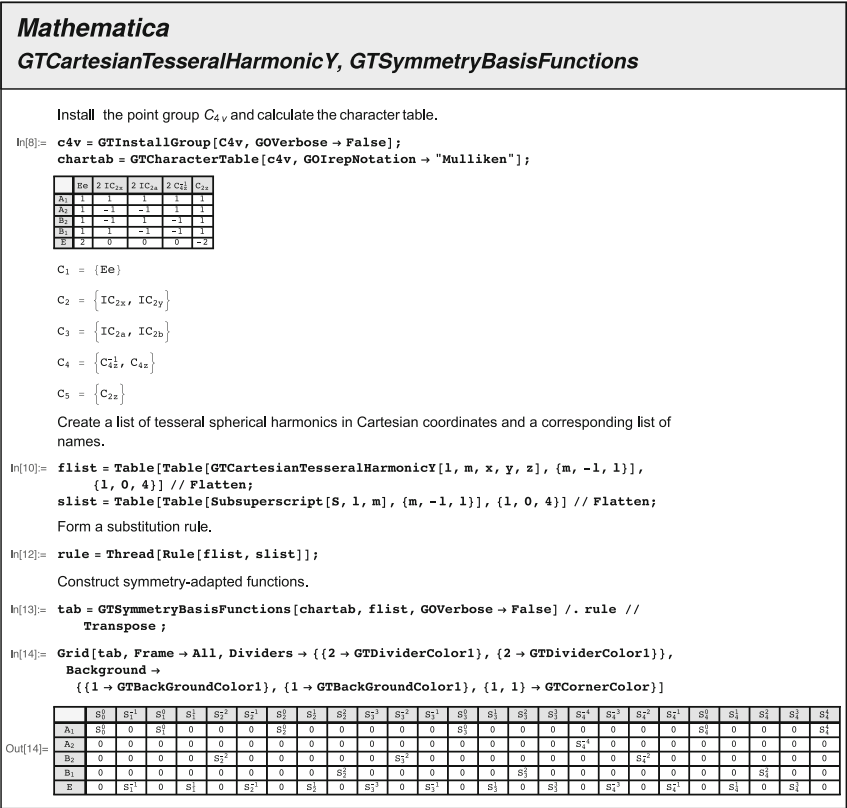


Figure 12.7 Tesseral spherical harmonics as basis functions of irreducible representations of the point group C_{4v} (corresponds to N-waves).

ample, basis functions of the totally symmetric representation A_1 are given by the functions S_l^0 . For the two-dimensional representation E , the basis functions can be identified to be $S_l^{\pm m}$ for odd values of m .

Example 60 (Symmetry-adapted vector spherical waves for O_h). Throughout the example it is shown, how to to construct symmetry-adapted vector spherical harmonics for the point group O_h using GTPack. For the calculation of M-waves, a sign change has to be taken into account for improper symmetry elements. This can be done by multiplying the characters of classes containing improper rotations by a factor of (-1) . The application of **GTSymmetryBasisFunctions** is illustrated in Figure 12.8. The procedure follows the previous example for the point group C_{4v} . The summarized results can be found in Table 12.2⁸⁾. In the next step, vector-spherical waves are constructed for the N -field. According to Figure 12.8, the spherical harmonics $Y_1^m(\theta, \varphi)$ as well as the corresponding tesseral spherical harmonics S_1^m are basis functions belonging to the irreducible representation T_{1u} . The N -field vector-spherical wave $E_{1,-1}^N$ is constructed from the scalar function $j_1 S_1^{-1}$ by applying $\hat{\mathbf{P}}^N$ as follows,

$$\begin{aligned} \mathbf{E}_{1,-1}^N &= \hat{\mathbf{P}}^N j_1(kr) S_1^{-1}(x, y, z), \quad r = \sqrt{x^2 + y^2 + z^2} \\ &= \frac{i}{k} \nabla \times \hat{\mathbf{L}} \left(j_1(kr) \cdot \sqrt{\frac{3}{4\pi}} \frac{y}{r} \right) \end{aligned} \quad (12.15)$$

Since S_1^{-1} is a basis function belonging to T_{1u} also $\mathbf{E}_{1,-1}^N$ is a basis function belonging to T_{1u} . Equation (12.15) can be evaluated using *Mathematica* giving the final result

$$\begin{aligned} \mathbf{E}_{1,-1}^N(x, y, z) &= \\ &= -\sqrt{\frac{3}{4\pi}} \frac{1}{r^2} \left\{ xy j_2(kr), \frac{2r^2 j_0(kr) - (x^2 - 2y^2 + z^2) j_2(kr)}{3}, yz j_2(kr) \right\}. \end{aligned} \quad (12.16)$$

Table 12.2 Correspondence between spherical harmonics of angular momentum l and irreducible representations of the point group O_h for M- and N-fields.

l	$2(l+1)$	M field	N field
1	3	T_{1g}	T_{1u}
2	5	E_u, T_{2u}	E_g, T_{2g}
3	7	A_{2g}, T_{1g}, T_{2g}	A_{2u}, T_{1u}, T_{2u}
4	9	$A_{1u}, E_u, T_{1u}, T_{2u}$	$A_{1g}, E_g, T_{1g}, T_{2g}$

8) The table agrees with the result given by OHTAKA and TANABE [194].

Mathematica

GTCartesianTesseralHarmonicY, GTSymmetryBasisFunctions

The character table of the group O_h was calculated before and the tables for M- and N-waves are stored in the lists ohctM and ohctN. A list of spherical harmonics in Cartesian coordinates and a corresponding list of names is created.

```
In[8]:= flist = Table[Table[GTCartesianSphericalHarmonicY[l, m, x, y, z], {m, -1, 1}],  
  {l, 1, 4}] // Flatten;
```

```
In[9]:= slist = Table[Table[Subsuperscript[Y, l, m], {m, -1, 1}], {l, 1, 4}] // Flatten;
```

Form a substitution rule.

```
In[10]:= rule = Thread[Rule[flist, slist]];
```

N-waves

Construct symmetry adapted functions.

```
In[11]:= tabN = GTSymmetryBasisFunctions[ohctN, flist, GOverbose -> False] /. rule;  
Do[Do[If[Head[tabN[[i, j]]] === Integer, None, tabN[[i, j]] = "x"]  
  , {i, 2, Length[flist] + 1}], {j, 2, 11}]
```

```
In[13]:= Grid[tabN // Transpose, Frame -> All,  
  Dividers -> {{2 -> GTDividerColor1}, {2 -> GTDividerColor1}},  
  Background -> {{1 -> GTBackGroundColor1},  
    {1 -> GTBackGroundColor1}, {1, 1} -> GTCornerRadiusColor}]
```

Out[13]=

	Y_1^{-1}	Y_1^0	Y_1^1	Y_2^{-2}	Y_2^{-1}	Y_2^0	Y_2^1	Y_2^2	Y_3^{-3}	Y_3^{-2}	Y_3^{-1}	Y_3^0	Y_3^1	Y_3^2	Y_3^3	Y_4^{-4}	Y_4^{-3}	Y_4^{-2}	Y_4^{-1}	Y_4^0	Y_4^1	Y_4^2	Y_4^3	Y_4^4
A _{1g}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	x	0	0	0	x	0	0	0	x
A _{2u}	0	0	0	0	0	0	0	0	x	0	0	0	x	0	0	0	0	0	0	0	0	0	0	0
A _{1u}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A _{2g}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
E _u	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
E _g	0	0	0	x	0	x	0	x	0	0	0	0	0	0	0	x	0	x	0	x	0	x	0	x
T _{1g}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	x	x	0	x	0	x	0	x	0	0
T _{2g}	0	0	0	x	x	0	x	x	0	0	0	0	0	0	0	x	x	0	x	x	0	x	x	0
T _{1u}	x	x	x	0	0	0	0	x	0	x	x	x	0	x	0	0	0	0	0	0	0	0	0	0
T _{2u}	0	0	0	0	0	0	0	0	x	x	x	0	x	x	0	0	0	0	0	0	0	0	0	0

M-waves

Construct symmetry adapted functions.

```
In[14]:= tabM = GTSymmetryBasisFunctions[ohctM, flist, GOverbose -> False] /. rule;  
Do[Do[If[Head[tabM[[i, j]]] === Integer, None, tabM[[i, j]] = "x"]  
  , {i, 2, Length[flist] + 1}], {j, 2, 11}]
```

```
In[16]:= Grid[tabM // Transpose, Frame -> All,  
  Dividers -> {{2 -> GTDividerColor1}, {2 -> GTDividerColor1}},  
  Background -> {{1 -> GTBackGroundColor1},  
    {1 -> GTBackGroundColor1}, {1, 1} -> GTCornerRadiusColor}]
```

Out[16]=

	Y_1^{-1}	Y_1^0	Y_1^1	Y_2^{-2}	Y_2^{-1}	Y_2^0	Y_2^1	Y_2^2	Y_3^{-3}	Y_3^{-2}	Y_3^{-1}	Y_3^0	Y_3^1	Y_3^2	Y_3^3	Y_4^{-4}	Y_4^{-3}	Y_4^{-2}	Y_4^{-1}	Y_4^0	Y_4^1	Y_4^2	Y_4^3	Y_4^4
A _{1g}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A _{2u}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
A _{1u}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	x	0	0	0	x	0	0	0	x
A _{2g}	0	0	0	0	0	0	0	0	x	0	0	0	x	0	0	0	0	0	0	0	0	0	0	0
E _u	0	0	0	x	0	x	0	x	0	0	0	0	0	0	0	x	0	x	0	x	0	x	0	x
E _g	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
T _{1g}	x	x	x	0	0	0	0	x	0	x	x	0	x	x	0	0	0	0	0	0	0	0	0	0
T _{2g}	0	0	0	0	0	0	0	0	x	x	0	x	x	x	0	0	0	0	0	0	0	0	0	0
T _{1u}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	x	x	0	x	x	0	x	x	0
T _{2u}	0	0	0	x	x	0	x	x	0	0	0	0	0	0	0	x	x	x	0	x	x	x	0	0

Figure 12.8 Symmetry-adapted vector spherical waves for point group O_h . ohctN is the character table of the point group, ohctM is the character table corrected to include the sign change for improper rotations. Spherical harmonics that contribute to a certain irreducible representation are marked by “x”.

Task 42 (Vector wave functions). Construct the vector spherical waves $\mathbf{E}_{1,-1}^N$, $\mathbf{E}_{1,0}^N$, and $\mathbf{E}_{1,1}^N$.

Part Four
Other Applications

13

Group Theory of Vibrational Problems

Whereas no chemist would these days treat, say, molecular vibrations without using the vocabulary of group theory, there is unfortunately, no elementary introduction to band theory of solids which adopt this approach. ... I felt, therefore that the time had now come to have a book which would bridge the gap between the current elementary texts and the more advanced treatments of the group theory of solid state.

S.L. Altmann
(*Band Theory of Solids*, Clarendon Press, 1991)

During the chapter vibrational modes within molecules and solids are discussed. Group theory can be used to classify the allowed vibrational modes entirely from the symmetry of the system. Furthermore, it can be determined which of the modes are active in RAMAN or infrared spectroscopy. In general, a nonlinear molecule of N atoms has a total of $3N$ degrees of freedom, where six of them describe the translation and the rotation of the molecule itself. Hence, $3N - 6$ vibrational modes remain. For solids, every atom in the unit cell gives rise to 3 phonon modes. In total, there are $3N$ phonon modes where three of them are acoustic modes and $3N - 3$ are optical modes.

13.1

Vibrations of Molecules

Vibrations of Molecules	
GTmolDatabaseInfo	Prints information stored within a molecular database
GTmolDatabaseUpdate	Adds new data to a molecular database
GTmolChemicalData	Imports molecular data from <i>Mathematica</i>
GTmolGetMolecule	Loads a molecular dataset from a database
GTmolToCluster	Exports structural information of a molecule as a cluster

GTVectorRep	Finds the vector representation for a given point group
GTVibDisplacementRep	Constructs the displacement representation
GTVibModeSymmetry	Gives the symmetry of the vibrational modes
GTVibSpectroscopy	Gives selection rules for IR and RAMAN spectroscopy

The center of the discussion for molecular vibrations lies in the invariance group, which can be determined from structural data. Using GTPack such data can be stored within a database. Commands to store to and retrieve data from databases are provided. During this section a few basic examples are given to illustrate the application of GTPack to vibrational problems. The theory behind these examples is extensively discussed in [36, 83, 203].

13.1.1

Permutation, Displacement, and Vector Representation

The starting point in the discussion of vibronic properties of a molecule is the symmetry of the molecule itself, having all atoms in equilibrium positions. The theory will be explained using the example of ammonia NH_3 with a molecular structure as plotted in Figure 13.1a. The threefold rotational axis passing through the nitrogen atom, together with the corresponding mirror planes of the molecule lead to a symmetry group G_0 , given by C_{3v} in this case, as shown in Figure 13.1b. All symmetry operations of C_{3v} leave the nitrogen atom at its position whereas the hydrogen atoms are permuted. These permutations of the atoms under symmetry operations of the invariance group C_{3v} can be used to construct a four-dimensional faithful representation in terms of permutation matrices, which is shown in Figure 13.2. It can be seen that C_{3z} and C_{3z}^{-1} cause a cyclic permutation of the hydrogen atoms whereas the three mirror operations leave the nitrogen atom and one hydrogen atom invariant.

The vibrations of molecules are discussed in terms of small deviations from the equilibrium positions. In general, a molecule contains N atoms. Thus, a total of

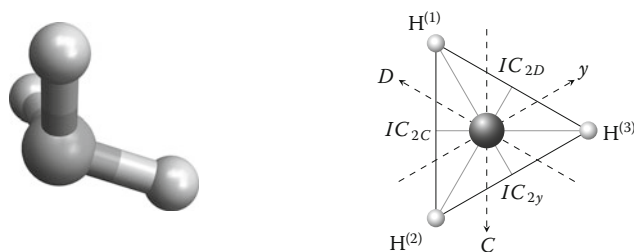


Figure 13.1 Structure and symmetry of the ammonia molecule NH_3 (from the *Mathematica* database with *GTmolChemicalData*). (a) Structure of the ammonia molecule; (b) C_{3v} symmetry of the ammonia molecule (top view).

Mathematica**GTmolDatabaseInfo, GTmolPermutationRep, GTVibDisplacementRep**

```
In[8]:= ammonia = GTmolGetMolecule["Molecules", 6]
```

```
Out[8]:= {Ammonia, NH3, NH3, C3v, Cornwell, Group Theory I, p. 174,
```

$$\{H, H, H, N\}, \left\{ \left\{ \frac{a}{\sqrt{3}}, 0, 0 \right\}, \left\{ -\frac{a}{2\sqrt{3}}, \frac{a}{2}, 0 \right\}, \left\{ -\frac{a}{2\sqrt{3}}, -\frac{a}{2}, 0 \right\}, \{0, 0, c\} \right\}$$

Calculation of the permutation representation.

```
In[9]:= GTmolPermutationRep[ammonia, GOverbose -> True];
```

Ee	C _{3z} ⁻¹	C _{3z}	IC _{2D}	IC _{2C}	IC _{2y}
$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$

Calculation of displacement representation. Example: C_{3z}⁻¹

```
In[10]:= dprep = GTVibDisplacementRep[ammonia, GOverbose -> True];
```

```
dmat = GTGetMatrix[C3zi]; dprmat = dprep[[2]];
gr1 = Grid[dprmat, Frame -> True,
```

Dividers -> {{4 -> Black, 7 -> Black, 10 -> Black},

{4 -> Black, 7 -> Black, 10 -> Black}}];

```
gr2 = Grid[dmat, Frame -> True];
Grid[{{gr1, " ", gr2}}]
```

0	0	0	0	0	0	0	$-\frac{1}{2}$	$-\frac{\sqrt{3}}{2}$	0	0	0	0
0	0	0	0	0	0	0	$\frac{\sqrt{3}}{2}$	$-\frac{1}{2}$	0	0	0	0
0	0	0	0	0	0	0	0	0	1	0	0	0
$-\frac{1}{2}$	$-\frac{\sqrt{3}}{2}$	0	0	0	0	0	0	0	0	0	0	0
$\frac{\sqrt{3}}{2}$	$-\frac{1}{2}$	0	0	0	0	0	0	0	0	0	0	0
0	0	1	0	0	0	0	0	0	0	0	0	0
0	0	0	$-\frac{1}{2}$	$-\frac{\sqrt{3}}{2}$	0	0	0	0	0	0	0	0
0	0	0	$\frac{\sqrt{3}}{2}$	$-\frac{1}{2}$	0	0	0	0	0	0	0	0
0	0	0	0	0	1	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	$-\frac{1}{2}$	$-\frac{\sqrt{3}}{2}$	0
0	0	0	0	0	0	0	0	0	0	$\frac{\sqrt{3}}{2}$	$-\frac{1}{2}$	0
0	0	0	0	0	0	0	0	0	0	0	0	1

$-\frac{1}{2}$	$-\frac{\sqrt{3}}{2}$	0
$\frac{\sqrt{3}}{2}$	$-\frac{1}{2}$	0
0	0	1

Figure 13.2 Permutation representation and displacement representation for the ammonia molecule NH₃.

3*N* generalized coordinates are introduced by

$$q_{k,1} = \sqrt{m_k} (x_k - x_k^0), \quad q_{k,2} = \sqrt{m_k} (y_k - y_k^0), \quad q_{k,3} = \sqrt{m_k} (z_k - z_k^0). \quad (13.1)$$

These displacements can be summarized as a column vector

$$\mathbf{q} = (q_{1,1}, q_{1,2}, q_{1,3}, q_{2,1}, \dots, q_{N,3}). \quad (13.2)$$

The transformation of a single displacement by a symmetry operation $T \in \mathcal{G}_0$ can be written as

$$\mathbf{r}'_j - \mathbf{r}^0_j = \underline{\underline{R}}(T) (\mathbf{r}_k - \mathbf{r}^0_k) . \quad (13.3)$$

Equation (13.3) means the equilibrium position of atom k is transformed to the equilibrium position of atom j , and the displacement of atom k is transferred to the displacement of atom j .

On the basis of the definition of the total displacement vector $\mathbf{q}$ in equation (13.2), the transformation of $\mathbf{q}$ to a vector $\mathbf{q}'$ by one of the operations of $\mathcal{G}_0$ can be expressed as

$$\mathbf{q}' = \underline{\underline{\Gamma}}^{\text{disp}}(T) \mathbf{q} , \quad (13.4)$$

where $\underline{\underline{\Gamma}}^{\text{disp}}(T)$ represents a $3N \times 3N$ -dimensional representation matrix related to the transformation $T \in \mathcal{G}_0$. Considering all $T \in \mathcal{G}_0$, then the matrices $\underline{\underline{\Gamma}}^{\text{disp}}(T)$ form a matrix representation that is called the *displacement representation* of $\mathcal{G}_0$. Figure 13.2 shows the displacement matrix together with the transformation matrix for the symmetry element C_{3z}^{-1} . The displacement representation itself can be found from the direct product of the permutation matrices $\underline{\underline{P}}(T)$ and the rotation matrices $\underline{\underline{R}}(T)$

$$\underline{\underline{\Gamma}}^{\text{disp}}(T) = \underline{\underline{P}}(T) \otimes \underline{\underline{R}}(T) . \quad (13.5)$$

In analogy to Theorem 25 of Section 5.5, it follows for the characters of the displacement representation¹⁾

$$\chi^{\text{disp}}(T) = \text{Tr } \underline{\underline{P}}(T) \text{Tr } \underline{\underline{R}}(T) . \quad (13.6)$$

The *vector representation* Γ^{vec} is defined to be the three-dimensional matrix representation of the invariance group $\mathcal{G}$, formed by rotation matrices describing the transformation of a vector $\mathbf{r}$ to a vector $\mathbf{r}'$,

$$\mathbf{r}' = \underline{\underline{R}}(T)\mathbf{r} . \quad (13.7)$$

For example, in the case of the group O_h this matrix representation is an irreducible representation of O_h (Γ^{15}, T_{1u}). However, this is not true in general as can be seen for C_{3v} , where the vector representation can be decomposed into the direct sum

$$\Gamma^{\text{vec}} = \Gamma_1 \oplus \Gamma_3 \quad (T_{1u} = A_1 \oplus E) . \quad (13.8)$$

In other words, the irreducible representations forming the vector representation are given by the ones containing the three functions $f_1 = x$, $f_2 = y$, and $f_3 = z$ as basis functions. For the point group O_h , x , y , and z are basis functions of the

1) Note that the statement of Theorem 25 also holds for any two representations of a group, which are not necessarily irreducible representations.

irreducible representation $\Gamma^{15}(T_{1u})$. For C_{3v} , z is a basis function to the identity representation $\Gamma_1(A_1)$, whereas x, y belong to the two-dimensional representation $\Gamma_3(E)$. Finally, in terms of representations, the displacement representation (13.5) can be written as the direct product of the permutation representation Γ^{per} and the vector representation Γ^{vec} ,

$$\Gamma^{\text{disp}} = \Gamma^{\text{per}} \otimes \Gamma^{\text{vec}}. \quad (13.9)$$

13.1.2

Vibrational Modes of Molecules

A nonlinear molecule of N atoms has a total of $3N$ degrees of freedom. Six of them describe the translation and the rotation of the molecule itself. It follows that $3N - 6$ vibrational modes remain²⁾. The displacement representation introduced within the previous section has a dimension of $3N$ and is in general a reducible representation of the invariance group of a molecule. It contains the symmetry of vibrational modes as well as the symmetry of the translational and rotational modes.

Example 61 (Decomposition of the displacement representation for an ammonia molecule). Following the example of the previous section, the decomposition of the displacement representation is performed for the ammonia molecule NH_3 having the point group C_{3v} . According to equation (13.9), the displacement representation Γ^{disp} can be expressed as the direct product of the permutation representation Γ^{per} and the vector representation Γ^{vec} . Applying Theorem 21 (cf. Section 5.3.4), the decomposition of Γ^{disp} in terms of irreducible representations of C_{3v} is given by

$$\Gamma^{\text{disp}} = 3A_1 \oplus A_2 \oplus 4E. \quad (13.10)$$

The same result can be obtained by decomposing Γ^{per} and Γ^{vec} first and evaluating the direct product in the second step,

$$\begin{aligned} \Gamma^{\text{disp}} &= \Gamma^{\text{per}} \otimes \Gamma^{\text{vec}} \\ &= (2A_1 \oplus E) \otimes (A_1 \oplus E) \\ &= 2A_1 \oplus 2E \oplus E \otimes E = 2A_1 \oplus 3E \oplus (A_1 \oplus A_2 \oplus E) \\ &= 3A_1 \oplus A_2 \oplus 4E. \end{aligned} \quad (13.11)$$

Within GTPack, the command **GTVibModeSymmetry** can be applied to decompose the displacement representation in terms of irreducible representations of the invariance group starting from the molecular structure only. Referring to the installation of a molecular structure in Figure 13.2, an example of the application of **GTVibModeSymmetry** is shown in Figure 13.3.

2) Linear molecules only possess two rotational degrees of freedom, i.e., $3N - 5$ vibrational modes exist.

Mathematica**GTVibModeSymmetry**

```
In[8]:= GTVibModeSymmetry[ammonia, GOIrepNotation -> "Mulliken"];
```

```
displacement representation:
```

```
6 matrices of dimension 12 x 12
```

```
characters disp. rep. : {12, 0, 2}
```

```
symmetry group      : C3v
```

	Ee	2 C _{3z} ⁻¹	3 IC _{2D}
A ₁	1	1	1
A ₂	1	1	-1
E	2	-1	0

```
C1 = {Ee}
```

```
C2 = {C3z-1, C3z}
```

```
C3 = {IC2D, IC2C, IC2y}
```

```
Reduction of direct product representation:
```

```
3 A1⊕A2⊕4 E
```

```
Ireps of rotations:
```

```
A2⊕E
```

```
Ireps of translations:
```

```
A1⊕E
```

```
2 A1⊕2 E
```

Figure 13.3 Decomposition of the displacement representation of the ammonia molecule NH₃.

Task 43 (Decomposition of displacement representation). Follow equation (13.11) and calculate the decomposition of the displacement representation into irreducible representations of C_{3v} for ammonia by decomposing the permutation representation and the vector representation first. Use GTPack commands.

To identify the irreducible representations belonging to the rotation and the translation of the molecule itself, it is necessary to calculate the characters of the translation and the rotation representation. Following [36], the following theorem is stated without proof.

Theorem 47 (Translation and rotation representation). Let $\chi^{tr}(T)$ and $\chi^{rot}(T)$ denote the characters of the translation representation Γ^{tr} and the rotation representation Γ^{rot} . For a nonlinear molecule, the characters $\chi^{tr}(T)$ and $\chi^{rot}(T)$ for a proper rotation $\underline{R}(T)$ through an angle θ are given by

$$\chi^{tr}(T) = \chi^{rot}(T) = 1 + 2 \cos \theta. \quad (13.12)$$

For an improper rotation it follows

$$-\chi^{tr}(T) = \chi^{rot}(T) = 1 + 2 \cos \theta \quad (13.13)$$

The characters of the rotation representation of a linear molecule (oriented along the x -axis) are given by

$$\chi^{rot}(T) = [\det \underline{\mathbb{R}}(T)] \sum_{k=2}^3 \underline{\mathbb{R}}(T)_{kk} . \quad (13.14)$$

By applying Theorem 47 to the ammonia molecule it can be verified that

$$I^{tr} = A_1 \oplus E \quad (13.15)$$

and

$$I^{rot} = A_2 \oplus E . \quad (13.16)$$

Thus, the symmetry of the vibrational modes of ammonia are given by $2A_1 \oplus 2E$ (see Figure 13.3). The dimensions of these irreducible representations correspond to the six vibrational degrees of freedom of the ammonia molecule.

The calculation of the displacements for the different modes will not be discussed here. The two A_1 modes of NH_3 are so-called breathing modes, where one of the modes describes an expansion and contraction of the H-triangle, while the nitrogen atom is at rest. The second mode with A_1 symmetry describes a motion of the H-triangle in the $+z$ -direction, while the nitrogen atom moves in the $-z$ -direction. In both cases, no translation of the center of mass occurs. The two E modes are doubly degenerate in-plane and out-of-plane modes. The analysis presented is referred to as normal mode analysis.

13.1.3

Infrared and Raman Activity

Allowed and forbidden transitions in infrared and RAMAN spectroscopy can be effectively analyzed by means of the WIGNER–ECKART Theorem (Theorem 27 in Section 5.6).³⁾ Transitions are allowed, if the integrals

$$M_{\text{IR}} = \int d^3 \mathbf{r} \Psi_i \underline{\mu} \Psi_f , \quad (13.17)$$

$$M_{\text{RAMAN}} = \int d^3 \mathbf{r} \Psi_i \underline{\alpha} \Psi_f , \quad (13.18)$$

are nonzero. The quantities $\underline{\mu}$ and $\underline{\alpha}$ are the induced dipole moment and the RAMAN polarizability tensor. The induced dipole moment is based on the atomic displacements and transforms like a vector. The RAMAN polarizability tensor is a

3) A comprehensive discussion can be found in [203].

second rank symmetric tensor. The initial state Ψ_i is determined by the equilibrium positions of the atoms in the molecule, i.e., it belongs to the totally symmetric irreducible representation of the invariance group of the molecule. The symmetry of possible final states Ψ_f is found by the normal mode analysis presented in Section 13.1.2. Applying the WIGNER–ECKART Theorem to equations (13.17) and (13.18) allows one to avoid the explicit evaluation of the integrals to determine if a transition is allowed.

The global symmetry of the system is given by the invariance group $\mathcal{G}_0$. To apply the WIGNER–ECKART Theorem, it has to be determined according to which irreducible representation the quantities $\underline{\mu}$ and $\underline{\alpha}$ transform. These irreducible representations have to have x , y , and z as basis functions in the case of infrared spectroscopy, as well as x^2 , y^2 , z^2 , xy , xz , and yz as basis functions in the case of RAMAN spectroscopy. Since the initial state always belongs to the totally symmetric irreducible representation, say Γ^1 , the direct product of Γ^q (describing the symmetry of components of $\underline{\mu}$ or $\underline{\alpha}$) with the irreducible representation Γ^p of the final state has to be analyzed. The state is allowed, if the direct product of Γ^q and Γ^p contains Γ^1 , otherwise it is forbidden,

$$\Gamma^q \otimes \Gamma^p \supseteq \Gamma^1 \quad \Rightarrow \quad \text{allowed} , \quad (13.19)$$

$$\Gamma^q \otimes \Gamma^p \not\supseteq \Gamma^1 \quad \Rightarrow \quad \text{forbidden} . \quad (13.20)$$

If Γ^q as a representation of a normal vibration mode of the molecule is equivalent to Γ^p of one of the components of $\underline{\mu}$ or $\underline{\alpha}$, the direct product always contains Γ^1 and represents an allowed transition.

The water molecule H_2O is the prototype molecule of type XY_2 having an invariance group C_{2v} . The normal mode analysis leads to $2A_1 \oplus B_2$. The analysis of the vector representation reveals for the components of $\underline{\mu}$: $\mu_x - B_1$, $\mu_y - B_2$, and $\mu_z - A_1$. Obviously, transitions to modes having A_1 or B_2 symmetry can be induced by μ_z and μ_y in IR spectroscopy.

Example 62 (Infrared and RAMAN activity of XeF_4). Xenontetrafluoride XeF_4 is a planar molecule with invariance group D_{4h} . The molecular structure is shown in Figure 13.4). The selection rules for the infrared and RAMAN activity of XeF_4 will be discussed by using the GTPack command **GTVibSpectroscopy**. A part of a *Mathematica* notebook is shown in Figure 13.5. The dataset for the molecule is extracted from the molecular database. In a first step the normal mode analysis is performed. The reduction of the displacement representation (15×15 matrices) leads after the removal of translations and rotations of the molecule itself to

$$\Gamma^{\text{disp}} \simeq A_{1g} \oplus B_{2g} \oplus A_{2u} \oplus B_{2u} \oplus B_{1g} \oplus 2E_u . \quad (13.21)$$

By specifying the option **GOSpecMode** it can be chosen whether the infrared or the RAMAN activity should be analyzed by **GTVibSpectroscopy**. In the case of infrared spectroscopy, the vector components x , y , and z form basis functions of the irreducible representations A_{2u} and E_u . Thus, normal modes according to A_{2u} and E_u are infrared active. The table for RAMAN activity indicates to

```
In[8]:= GTMolToCluster[XeF4]
```

```
minimal distance : 195.  
maximal distance : 390.
```

```
F ■  
Xe ■
```

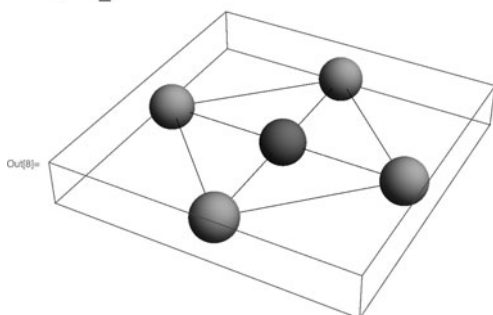


Figure 13.4 Structure of the planar XeF_4 molecule with D_{4h} symmetry.

Mathematica

GTVibModeSymmetry, GTVibSpectroscopy

```
In[8]:= vibmodes =  
GTvibModeSymmetry[XeF4, GOIrepNotation -> "Mulliken", GOverbose -> False]
```

```
A1g ⊕ B2g ⊕ A2u ⊕ B2u ⊕ B1g ⊕ 2 Eu
```

```
Out[8]:= {1, 0, 1, 1, 1, 0, 0, 1, 2, 0}
```

```
In[9]:= GTvibSpectroscopy[{1, 3, 4, 5, 8, 9}, d4hct, GOSpecMode -> "InfraRed"]
```

```
Dipole in Ireps : {A2u, Eu}
```

$\Gamma(\mu_k)$	component	allowed mode
A _{2u}	{z}	A _{2u}
E _u	{x, y}	E _u

```
In[10]:= GTvibSpectroscopy[{1, 3, 4, 5, 8, 9}, d4hct, GOSpecMode -> "Raman"]
```

```
Polarizability in Ireps : {A1g, B2g, B1g, Eg}
```

$\Gamma(\alpha_{ij})$	component	allowed mode
A _{1g}	{x ² , y ² , z ² }	A _{1g}
B _{2g}	{x y}	B _{2g}
B _{1g}	{x ² , y ² }	B _{1g}

Figure 13.5 Infrared and RAMAN selection rules for Xenontetrafluoride XeF_4 investigated using GTvibSpectroscopy.

which irreducible representations the independent components of $\underline{\alpha}$ belong. More precisely, the symmetrized basis functions are $(x^2 + y^2)/2$ and z^2 in the case of A_{1g} and $\pm(x^2 - y^2)/2$ for B_{1g} , if basis functions are constructed, starting from x^2, y^2, z^2 .⁴⁾

4) This can be verified easily by means of GTSymmetryBasisFunctions.

13.2
Lattice Vibrations

Lattice vibrations	
GTVibTbToPhonon	Transforms a TB-Hamiltonian into a dynamical matrix
GTVibTbToPhononRule	Gives rules to transform a tight-binding p -Hamiltonian into a dynamical matrix
GTVibDynamicalMatrix	Constructs a dynamical matrix from a spring model
GTVibSetParameters	Sets parameters for a dynamical matrix
GTVibLatticeModes	Performs an analysis of zone center modes

The complete Hamiltonian of a solid describes a complex many-body problem. The adiabatic approximation (BORN–OPPENHEIMER approximation) is used to separate the electron system from the much slower movement of the nuclei. Within this approximation, the total energy and the energy spectrum of the electrons is calculated for fixed positions of the nuclei. The solution itself can be done, for example, in the framework of *ab initio* methods, based on density functional theory (DFT) or by means of model Hamiltonians. In Chapter 9, the application of symmetry arguments to electronic structure problems was discussed. Now, the focus lies on the motion of the nuclei.⁵⁾ A classical HAMILTON function for N particles (point masses) given by

$$H = \sum_{k=1}^N \frac{\mathbf{p}_k^2}{2M_k} + V_{\text{eff}}(\mathbf{R}_1, \dots, \mathbf{R}_N) . \tag{13.22}$$

will be investigated. The effective interaction potential V_{eff} depends on all coordinates $\mathbf{R}_k$ of the nuclei. Small deviations from equilibrium positions will be considered. The potential is minimized for the equilibrium positions of the nuclei. Expanding the potential up to second order (harmonic approximation) and using the ansatz⁶⁾

$$\mathbf{R}_k = \mathbf{R}_k^0 + \mathbf{u}_k , \tag{13.23}$$

gives

$$\begin{aligned} V_{\text{eff}}(\mathbf{R}_1, \dots, \mathbf{R}_N) = V(\mathbf{R}^{(0)}) &+ \sum_{k\alpha} \left. \frac{\partial V}{\partial R_{k\alpha}} \right|_{\mathbf{R}^{(0)}} u_{k\alpha} \\ &+ \frac{1}{2} \sum_{k\alpha, n\beta} \left. \frac{\partial^2 V}{\partial R_{k\alpha} \partial R_{n\beta}} \right|_{\mathbf{R}^{(0)}} u_{k\alpha} u_{n\beta} \end{aligned} \tag{13.24}$$

The indices α, β denote the components of the vectors $\mathbf{R}_k, \mathbf{R}_n$. The first term $V(\mathbf{R}^{(0)})$ can be neglected within the discussion since it describes a constant in

5) See also [204, 205] for details. The examples within this section follow the discussion of [206].
6) $\mathbf{R}^{(0)}$ is the set of all equilibrium positions, i.e., $\mathbf{R}^{(0)} = (\mathbf{R}_1^{(0)}, \dots, \mathbf{R}_N^{(0)})$.

energy (rigid shift of the energy scale). Furthermore, the first derivative of V with respect to $\mathbf{R}$ is zero at $\mathbf{R}^{(0)}$ since V has its minimum at $\mathbf{R}^{(0)}$. Following (13.24), the force constant matrix $\underline{\Phi}$ and the dynamical matrix $\underline{D}$ can be defined via

$$\Phi_{k\alpha,n\beta} = \left. \frac{\partial V^2}{\partial R_{k\alpha} \partial R_{n\beta}} \right|_{\mathbf{R}^{(0)}}, \quad D_{k\alpha,n\beta} = \frac{1}{\sqrt{M_k M_n}} \Phi_{k\alpha,n\beta}. \quad (13.25)$$

Both matrices are $dN \times dN$ -dimensional (d is the spatial dimension), real, symmetric, and positive definite. A unitary transformation of the initial HAMILTON function with the effective harmonic potential leads to the HAMILTON function in harmonic approximation

$$H_{\text{harm}} = \frac{1}{2} \sum_{i=1}^{dN} \left(\bar{p}_i^2 + \omega_i^2 \bar{u}_i^2 \right). \quad (13.26)$$

The diagonalization of the dynamical matrix provides the frequencies ω_i .

In a perfect solid lattice translational periodicity is present. The solid is characterized by a BRAVAIS lattice having lattice vectors $\mathbf{t}_k$ and a basis of r atoms at positions $\boldsymbol{\tau}_\mu$ ($\mu = 1, \dots, r$) in the unit cell. Thus, the vectors $\mathbf{t}_k + \boldsymbol{\tau}_\mu$ point to the equilibrium positions of the atoms. The actual position of the μ th atom in the k th unit cell including a small displacement $\mathbf{u}_{k\mu}$ can be expressed as

$$\mathbf{R}_{k\mu} = \mathbf{t}_k + \boldsymbol{\tau}_\mu + \mathbf{u}_{k\mu}. \quad (13.27)$$

The potential is given as

$$V = \frac{1}{2} \sum_{k\mu\alpha, n\nu\beta} \left. \frac{\partial V^2}{\partial R_{k\mu\alpha} \partial R_{n\nu\beta}} \right|_{eq.} u_{k\mu\alpha} u_{n\nu\beta}, \quad (13.28)$$

$$= \frac{1}{2} \sum_{k\mu\alpha, n\nu\beta} \Phi_{k\mu\alpha, n\nu\beta} u_{k\mu\alpha} u_{n\nu\beta}. \quad (13.29)$$

Expressing a force via the gradient of the potential, $\mathbf{F} = -\nabla V$, it is possible to formulate classical equations of motion (NEWTONS equation of motion) including the force constant matrix $\underline{\Phi}$,

$$M_\mu \ddot{u}_{k\mu\alpha} = - \sum_{n\nu\beta} \Phi_{k\mu\alpha, n\nu\beta} u_{n\nu\beta}. \quad (13.30)$$

The translational symmetry together with the harmonic approximation allow for the following ansatz of the solution

$$u_{k\mu\alpha} = v_{\mu\alpha} e^{i(\mathbf{q} \cdot \mathbf{t}_k - \omega t)}. \quad (13.31)$$

Using ansatz (13.31) in (13.30), the following eigenvalue equation allows one to calculate the spectrum of the vibrational modes,

$$\omega^2 v_{\mu\alpha} = \sum_{\nu\beta} D_{\mu\alpha, \nu\beta}(\mathbf{q}) v_{\nu\beta}, \quad (13.32)$$

$$D_{\mu\alpha, \nu\beta}(\mathbf{q}) = \sum_{\mathbf{t}_k} D_{\mu\alpha, \nu\beta}(\mathbf{t}_k) e^{-i\mathbf{q} \cdot \mathbf{t}_k},$$

where $D_{\mu\alpha, \nu\beta}(\mathbf{q})$ is the FOURIER transform of the dynamical matrix. The FOURIER transformation of the dynamical matrix reduces the dimension drastically from $dNr \times dNr$ to $dr \times dr$. The $d \cdot r$ eigenmodes are classified in terms of d acoustic phonon modes and $d(r - 1)$ optical phonon modes. The GTPack tools developed for the discussion of band structures in $\mathbf{k}$ -space (electronic band structures, photonic band structures) can be applied to investigate phonons in a similar way. The central point is the formulation of a reasonable potential. From the potential itself the dynamical matrix can be calculated. The eigenvalues of the FOURIER transformed dynamical matrix $\underline{\underline{D}}(\mathbf{q})$ provide the phonon bands $\omega_i(\mathbf{q})$.

13.2.1

Direct Calculation of the Dynamical Matrix

In a simple model for lattice vibrations the interaction between atoms is mediated by strings of a certain strength k_s . Here, s is the number of included neighboring shells. The total number of included k_s determines how far the interactions reach. The interaction potential between the atoms at the positions $\mathbf{r}_k$ and $\mathbf{r}_n$ in the unit cell is given by

$$\begin{aligned} V_{kn} &= \frac{k}{2} (|\mathbf{r}_k + \mathbf{u}_k - \mathbf{r}_n - \mathbf{u}_n| - |\mathbf{r}_k - \mathbf{r}_n|)^2 \\ &\approx \frac{k}{2} \left(\frac{(\mathbf{r}_k - \mathbf{r}_n)}{|\mathbf{r}_k - \mathbf{r}_n|} \cdot (\mathbf{r}_k - \mathbf{r}_n) \right)^2 \end{aligned} \quad (13.33)$$

Example 63 (Phonon band structures for the simple cubic lattice). The dynamical matrix will be calculated for a hypothetical material having a simple cubic lattice and one atom in the unit cell. Within GTPack, the dynamical matrix can be constructed starting from a potential (13.33) using **GTvibDynamicalMatrix**. An example is shown in Figure 13.6. To replace parameters within the dynamical matrix by actual numerical values for the spring strengths and masses, **GTvibSetParameters** can be used. In the present case, interactions with nearest and next nearest neighbors are taken into account. The spring constants and the mass are chosen to be

$$k_1 = 1, \quad k_2 = 0.5, \quad m = 1. \quad (13.34)$$

To solve the eigenvalue problem itself, **GTBandStructure** can be applied as shown before in connection to electronic or photonic band structures. Note that similar to the photonic problem, following from (13.32), the eigenvalue is actually given by ω^2 , i.e., the option **GOPhotonic** has to be set True.

Mathematica**GTVibDynamicalMatrix, GTVibSetParameters**

Construction of the dynamical matrix using **GTVibDynamicalMatrix** for a simple cubic lattice. A cut-off radius of 3 is chosen and 2 shells are taken into account.

```
In[8]:= ham = GTVibDynamicalMatrix[{{1, 0, 0}, {0, 1, 0}, {0, 0, 1}}, 3, 2, GVerbose -> False]
```

Number of shells : 9

```
Out[8]:= {{ 1/m (4 Sin[π ξ]^2 k1 -  

  (-4 + Cos[2 π (ξ - ξ)] + Cos[2 π (η - ξ)] + Cos[2 π (ξ + ξ)] + Cos[2 π (η + ξ)]) k2),  

  2 Sin[2 π η] Sin[2 π ξ] k2, 2 Sin[2 π ξ] Sin[2 π ξ] k2),  

  { 2 Sin[2 π η] Sin[2 π ξ] k2, 1/m (4 Sin[π η]^2 k1 -  

  (-4 + Cos[2 π (ξ - η)] + Cos[2 π (ξ + η)] + Cos[2 π (η - ξ)] + Cos[2 π (η + ξ)]) k2),  

  2 Sin[2 π ξ] Sin[2 π η] k2), { 2 Sin[2 π ξ] Sin[2 π ξ] k2,  

  2 Sin[2 π ξ] Sin[2 π η] k2, 1/m (4 Sin[π ξ]^2 k1 -  

  (-4 + Cos[2 π (ξ - η)] + Cos[2 π (ξ + η)] + Cos[2 π (ξ - ξ)] + Cos[2 π (ξ + ξ)]) k2)}}
```

Set the spring constants and the mass. The spring constant for the first and second shell are chosen to be 1 and 0.5, respectively. The mass is chosen to be 1.

```
In[9]:= hamp = GTVibSetParameters[ham, {1, 0.5}, {1}]
```

```
Out[9]:= {{ -0.5 (-4 + Cos[2 π (ξ - ξ)] + Cos[2 π (η - ξ)] + Cos[2 π (ξ + ξ)] + Cos[2 π (η + ξ)]) +  

  4 Sin[π ξ]^2, 1. Sin[2 π η] Sin[2 π ξ],  

  1. Sin[2 π ξ] Sin[2 π ξ]}, {1. Sin[2 π η] Sin[2 π ξ],  

  -0.5 (-4 + Cos[2 π (ξ - η)] + Cos[2 π (ξ + η)] + Cos[2 π (η - ξ)] + Cos[2 π (η + ξ)]) +  

  4 Sin[π η]^2, 1. Sin[2 π ξ] Sin[2 π η]},  

  {1. Sin[2 π ξ] Sin[2 π ξ], 1. Sin[2 π ξ] Sin[2 π η],  

  -0.5 (-4 + Cos[2 π (ξ - η)] + Cos[2 π (ξ + η)] + Cos[2 π (ξ - ξ)] + Cos[2 π (ξ + ξ)]) +  

  4 Sin[π ξ]^2}}
```

Calculate the phonon spectrum using **GTBandStructure**.

```
In[10]:= kpath = GTBzPath["sc"];
```

```
GTBandStructure[hamp, kpath, 30, 3,
```

```
Joined -> True, GPhotonic -> True, PlotLabel -> " ",
```

```
FrameLabel -> {" ", "ħω (arb. units)", PlotRange -> Full, PlotStyle -> Black]
```

Maximum Abscissa = 3.57313

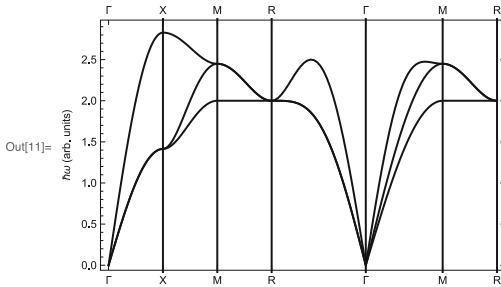


Figure 13.6 Construction of the dynamical matrix and calculation of the phonon spectrum for a simple cubic lattice within GTPack.

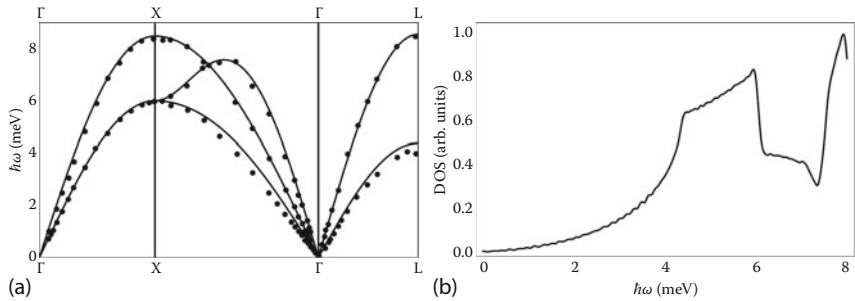


Figure 13.7 Phonon band structure and density of states for crystalline argon in an fcc structure calculated using **GTVibDynamicalMatrix**, **GTBandStructure** and **GTDensityOf-**

States ($k_1 = 9.0, k_2 = 0.3, m = 1$). (a) Phonon band structure. Dots show experimental values according to [207]. (b) Phonon density of states.

Example 64 (Phonon spectrum for crystalline argon). The noble gas argon crystallizes below temperatures of 83.81 K in an fcc lattice. The lattice vectors for the fcc structure are given by

$$\mathbf{a}_1 = \frac{a}{2}(1, 1, 0), \quad \mathbf{a}_2 = \frac{a}{2}(0, 1, 1), \quad \mathbf{a}_3 = \frac{a}{2}(1, 0, 1), \quad (13.35)$$

where the lattice constant for argon is given by $a = 5.25 \text{ \AA}$ [208]. Within the GT-Pack example, the units are renormalized to $a = 1$ and $m = 1$. The spring constants for the nearest and next nearest neighbor interactions were fitted such that the experimental spectrum is revealed.

The dynamical matrix is formulated by using **GTVibDynamicalMatrix** similarly to Example 63. From the dynamical matrix, the band structure and density of states is calculated using **GTBandStructure** and **GTDensityOfStates**, respectively. The result is shown in Figure 13.7.

13.2.2

Dynamical Matrix from Tight-Binding Models

The construction of tight-binding Hamiltonians in two-center form was discussed in Section 9.4.1. Subsequently, it is shown how the formalism can be used for the calculation of phonon spectra of solids.⁷⁾ In general, a solid with N atoms within the primitive unit cell reveals three phonon modes per atom. In total, three modes are acoustic modes and $3N - 3$ modes are optical modes. Thus, a solid with one atom per primitive cell exhibits three acoustic modes and a binary compound three acoustic and three optical modes.

The dynamical matrix within the central force model for the interaction of atoms is constructed from a tight-binding Hamiltonian for p -orbitals. The dynamical matrix itself is revealed by identifying the hopping parameters of the

7) The discussion follows remarks in [137], p. 404f.

tight-binding model with the corresponding expressions for the dynamical matrix. The $(pp\sigma)$ -parameters represent the direct interaction of two atoms and have to be substituted by k/m . Since there is no interaction in the central force model corresponding to the $(pp\pi)$ -parameters, the $(pp\pi)$ -parameters will be set to zero. These substitution rules can be generated automatically by the command **GTVibTbToPhononRule**.⁸⁾ Special attention has to be paid to on-site elements $(pp0)$. In contrast to the tight-binding Hamiltonian there exists no independent on-site parameter for the case of the dynamical matrix. For example, after substituting the hopping parameters, the modified matrix at the Γ point of the Brillouin zone for an fcc structure including interactions up to next nearest neighbors is given by

$$\begin{pmatrix} (pp0) + 4\frac{k_1}{m} + 2\frac{k_2}{m} & 0 & 0 \\ 0 & (pp0) + 4\frac{k_1}{m} + 2\frac{k_2}{m} & 0 \\ 0 & 0 & (pp0) + 4\frac{k_1}{m} + 2\frac{k_2}{m} \end{pmatrix}. \quad (13.36)$$

Here, the sum rules of the force constant matrix lead to the substitution

$$(pp0) \rightarrow -4\frac{k_1}{m} - 2\frac{k_2}{m}. \quad (13.37)$$

This substitution leads to the zero frequency modes of the acoustic branches at the zone center. Within GTPack, a tight-binding Hamiltonian for p -orbitals can be transformed into a dynamical matrix by applying **GTVibTbToPhonon**. Numerical values for the parameters can be included using **GTVibSetParameters**. For the actual band structure calculation, **GTBandStructure** can be used. An example for a monoatomic fcc structure is shown in Figure 13.8.

13.2.3

Analysis of Zone Center Modes

Classifying the zone center modes of phonon band structures for crystals follows a similar strategy as determining the normal modes of molecules. At the Γ point ($\mathbf{k} = 0$), all points separated by a lattice vector $\mathbf{t}_n$ are considered to be equal, since no phase shifts due to BLOCH factors appear. The vibrational modes of the lattice are calculated in analogy to molecules, where the allowed normal modes are found from: $\Gamma^{\text{vib,mol}} = \Gamma^{\text{per}} \otimes \Gamma^{\text{vec}} - \Gamma^{\text{trans}} - \Gamma^{\text{rot}}$. In the case of a crystal the representation

$$\Gamma^{\text{vib,latt}} = \Gamma^{\text{per}} \otimes \Gamma^{\text{vec}} \quad (13.38)$$

is used, where the irreducible representations for rotations and translations are not subtracted. The lattice periodic solid is considered to be fixed in space and no rotational degrees of freedom occur. The translational degrees of freedom correspond to the three acoustic branches at $\mathbf{k} = 0$.

8) **GTVibTbToPhononRule** is included within the command **GTVibTbToPhonon** and does not need to be called explicitly.

Mathematica

GTVibTbToPhononRule, GTVibTbToPhonon, GTVibSetParameters

The tight-binding Hamiltonian for a fcc-structure using p-orbitals was constructed before and saved to the file `fcc_p.ham`. Using `GTReadFromFile` this Hamiltonian is loaded.

```
In[8]:= tb = GTReadFromFile["fcc_p.ham"]; tb[[1, 1]]
Out[8]:= (pp0) + 2 ((Cos[π η] Cos[π ξ] + Cos[π ξ] (Cos[π η] + 2 Cos[π ξ])) (ppπ)1 +
Cos[π η] (Cos[π ξ] + Cos[π ξ]) (ppσ)1) +
2 ((Cos[2 π ξ] + Cos[2 π η]) (ppπ)2 + Cos[2 π η] (ppσ)2)
```

Generate the substitution rule for the hopping parameters.

```
In[9]:= GTVibTbToPhononRule[{2}]
Out[9]:= {(ppπ)1 → 0, (ppσ)1 → - $\frac{k_1}{m}$ , (ppπ)2 → 0, (ppσ)2 → - $\frac{k_2}{m}$ }
```

Transform the tight-binding Hamiltonian into a dynamical matrix using `GTVibTbToPhonon`.

```
In[10]:= dynm = GTVibTbToPhonon[tb, {2}, GVerbose → False];
```

The spring constants for nearest and next nearest neighbor interaction are chosen to be 1.0 and 0.1, respectively. The mass is set to 1.

```
In[11]:= dynmp = GTVibSetParameters[dynm, {1.0, 0.1}, {1}];
```

The phonon band structure is calculated using `GTBandStructure`.

```
In[12]:= kpath = GTBZPath["fcc"]; GTBandStructure[dynmp, kpath, 50, 3, Joined → True,
GPhotonic → True, PlotLabel → "", FrameLabel → {"", "ħω (arb. units)"},
PlotRange → {{0, 4.49}, {0, 3}}, PlotStyle → Black]
Maximum Abscissa = 4.48735
```

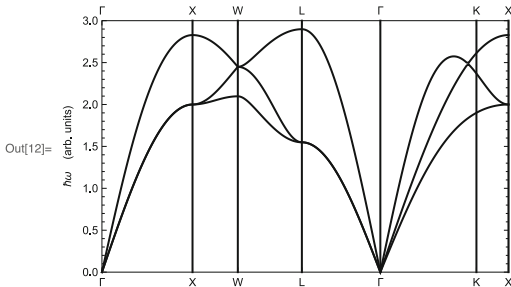


Figure 13.8 Calculation of the phonon band structure for a fcc lattice within the central force model from a tight-binding p -Hamiltonian.

Example 65 (Zone center modes for cubic crystals). In the following, the symmetry of zone center modes is discussed using the example of cubic crystals. In Figure 13.9, a `GTPack` example is shown for the perovskite BaTiO_3 , where the command `GTVibLatticeModes` is applied. Analogously to `GTVibModeSymmetry`, `GTVibLatticeModes` automatically constructs the representation Γ^{vib} and performs a decomposition into irreducible representations of the underlying symmetry group according to Theorem 21. In the case of BaTiO_3 , the dimension

Mathematica**GTVibLatticeModes**

```

Load the crystal structure for BaTiO3

In[8]:= GTLoadStructures["GTPack"]; bto = GTGetStructure[7]

1 structure found in spegrp.

-----

Out[8]:= {{BTO, Perovskite}, cP5, E21, Pm $\bar{3}$ m, 221,
  {{a, 0, 0}, {0, a, 0}, {0, 0, a}}, {{0, 0, 0}, Ti}, {{ $\frac{a}{2}$ ,  $\frac{a}{2}$ ,  $\frac{a}{2}$ }, Ba},
  {{ $\frac{a}{2}$ , 0, 0}, 0}, {{0,  $\frac{a}{2}$ , 0}, 0}, {{0, 0,  $\frac{a}{2}$ }, 0}}, {a → 361.49}}

Calculate the zone center modes

In[9]:= GTVibLatticeModes[bto, 1, Oh, GOLattice → {a → 1}, GOTbEquivalence → False,
  GOIrepNotation → "Mulliken", GOVerbose → False];

21 atoms

Atoms in cluster: {{Ba1, 8}, {Ti1, 7}, {O3, 2}, {O2, 2}, {O1, 2}}

Equivalence representation :

3 A1g ⊕ Eg

Vector representation :

T1u

Lattice Modes :

4 T1u ⊕ T2u

```

Figure 13.9 Construction of zone center modes for BaTiO₃.

of the permutation representation is given by 5. The representation is reducible with respect to the irreducible representations of O_h leading to the direct sum

$$\Gamma_{\text{BaTiO}_3}^{\text{per}} \simeq 3A_{1g} \oplus E_g. \quad (13.39)$$

The vector representation for O_h is given by the irreducible representation T_{1u} . Hence, it follows

$$\Gamma_{\text{BaTiO}_3}^{\text{vib,lat}} \simeq (3A_{1g} \oplus E_g) \otimes T_{1u} = 4T_{1u} \oplus T_{2u}. \quad (13.40)$$

The 5 atoms in the BaTiO₃ unit cell give rise to 15 modes, 3 acoustical modes and 12 optical modes. The optical modes at the zone center of BaTiO₃ belong to three T_{1u} representations and a T_{2u} representation.

For the monoatomic fcc system Cu, the permutation representation is one-dimensional and equivalent to the totally symmetric representation of O_h , A_{1g} . As T_{1u} is the vector representation, it follows for $\Gamma_{\text{Cu}}^{\text{vib}}$,

$$\Gamma_{\text{Cu}}^{\text{vib,lat}} \simeq A_{1g} \otimes T_{1u} = T_{1u}. \quad (13.41)$$

Hence, at the Γ point, only the three degenerated acoustic modes to $\omega = 0$ exist, corresponding to the irreducible representation T_{1u} .

NaCl and ZnSe are systems having two atoms in the unit cell. Therefore, besides the acoustic modes, three optical modes appear. The point group symmetry at Γ is given by O_h for NaCl and by T_d for ZnSe. A summary of the symmetry of the zone center modes for the four discussed cubic structures can be found in Table 13.1.

Table 13.1 Zone center modes for cubic structures (B – BOUCKAERT notation, M – MULLIKEN notation).

System	PG	Permutation rep.		Vector rep.		Zone center modes	
		B	M	B	M	B	M
Cu	O_h	Γ_1	A_{1g}	Γ_{15}	T_{1u}	Γ_{15}	T_{1u}
BaTiO ₃	O_h	$3\Gamma_1 \oplus \Gamma_{12}$	$3A_{1g} \oplus E_g$	Γ_{15}	T_{1u}	$4\Gamma_{15} \oplus \Gamma_{25}$	$4T_{1u} \oplus T_{2u}$
NaCl	O_h	$2\Gamma_1$	$2A_{1g}$	Γ_{15}	T_{1u}	$2\Gamma_{15}$	$2T_{1u}$
ZnSe	T_d	$2\Gamma_1$	$2A_1$	Γ_{15}	T_2	$2\Gamma_{15}$	$2T_2$

14

Landau Theory of Phase Transitions of the Second Kind

Was wir mathematisch festlegen ist nur zum kleinen Teil ein objektives Faktum, zum größeren Teil eine Übersicht über Möglichkeiten.

*W. Heisenberg
(Schritte über Grenzen, Piper 1976)*

Symmetry and symmetry breaking are basic concepts within the discussion of second-order phase transitions. The theory of changing symmetry within a phase transition was initially described by L.D. LANDAU. This chapter describes second-order phase transitions by LANDAU's phenomenological theory. At second-order phase transitions the symmetry of the system is decreased and the emerging phase is characterized by a so-called order parameter. The chapter gives a short introduction to the application of group theory to second-order phase transitions. It introduces the concept for a specific example of a structural phase transition within a crystal. Afterwards, the chapter generalizes the theory and discusses the abstract group theoretical description. The LANDAU and the LIFSHITZ criterion are based on the anti-symmetrized third power and the symmetrized second power of a representation. The discussion of both criteria by means of GTPack commands is demonstrated.

Symmetry and symmetry breaking are basic concepts within the discussion of second-order phase transitions. The theory of changing symmetry within a phase transition was initially described by L.D. LANDAU. A series of books [210–212] and original papers (see, e.g., [213–216]) discuss the theory in great detail and connect it to the application of group theory. Well-known examples are the ferroelectric phase transition in BaTiO_3 , or the superconducting phase transition [217–221]. During the last decades extensions of the theory to aperiodic systems (modulated phases, incommensurable composites, quasicrystals) were investigated [222, 223]. Within these systems, the symmetry is not described in terms of space groups, but of supergroups in a higher dimensional space. However, a reconsideration of LANDAU's theory leads to phase transitions with changes of the supergroup dimension and to transitions without such a change.

14.1

Introduction to Landau’s Theory of Phase Transitions

To begin with, a structural phase transition will be used as an example to discuss the basic ideas of LANDAU’s theory¹⁾. The structure under consideration is a body-centered tetragonal structure, as illustrated in Figure 14.1. It has one atom denoted by A at the corners²⁾ of the unit cell as well as one central atom denoted by B. The structural phase transition occurs at temperature T_0 and pressure P_0 , where for temperatures $T > T_0$ the B atom is located at the inversion center of the unit cell,

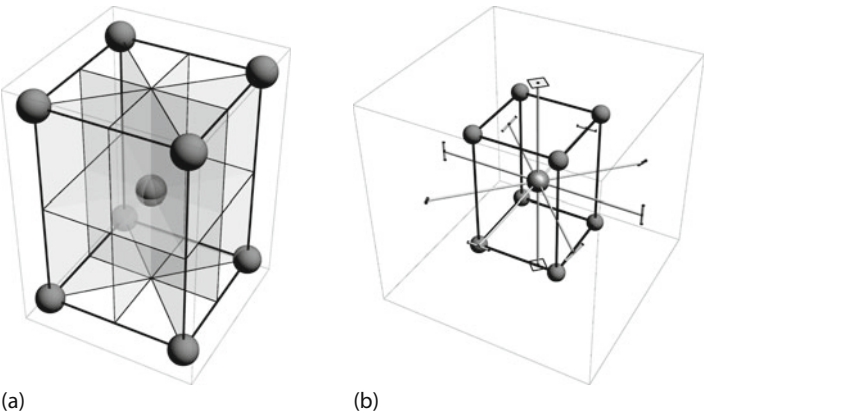


Figure 14.1 Body-centered tetragonal structure with symmetry elements. The A-atoms are located at the corners of the unit cell, while the B atom is located at the inversion center. (Plots to illustrate the reflection planes and rotation axes of D_{4h} can be obtained using `GTShowSymmetryElements`). (a) Reflection planes; (b) rotation axes.

Mathematica

GTSymmetryElementQ

An artificial tetragonal structure is used.

In[17]:= `str = {{ "AB", "bct"}, {"tI2", "Aa", "I4/mmm", 139, {{a, 0, 0}, {0, a, 0}, {0, 0, 2 a}}, {{0, 0, 0}, "A"}}, {pos, "B"}}, {a -> 1}}; pos = {a / 2, a / 2, a};`

Create a cluster of atoms.

In[18]:= `cl = GTCluster[str, 2, GOLattice -> {a -> 1}];`

39 atoms

Atoms in cluster: {{B, 24}, {A, 15}}

Install the group D_{4h} and analyse if it is the symmetry group of the cluster.

In[19]:= `d4h = GTInstallGroup[D4h, GOverbose -> False]; GTSymmetryElementQ[d4h, cl]`

Out[19]= True

Figure 14.2 Application of `GTSymmetryElementQ` to show that the point group of the body-centered tetragonal lattice is given by D_{4h} .

1) The example follows the line of chapter I in [210], by applying GTPack.

2) Corner atoms are counted by a weight of 1/8.

while for $T < T_0$ it moves out of this position and the symmetry is lowered. The point group of the high-temperature structure is given by D_{4h} . Within GTPack, this can be verified by installing an artificial body-centered tetragonal structure and generating an atomic cluster by means of **GTCluster**. By applying **GTSymmetryElementQ** it can be checked if the atomic cluster is invariant under the symmetry transformations associated with D_{4h} . An example is shown in Figure 14.2.

Considering the low-temperature structure, the shift of the central atom B is denoted by $\mathbf{p}$. Each possible shift breaks certain symmetries of D_{4h} . Therefore, the resulting structure belongs to a subgroup of D_{4h} . Again, by applying **GTSymmetryElementQ** it can be checked which symmetry elements remain if a certain vector $\mathbf{p}$ is present. Figure 14.3 shows all possible vectors $\mathbf{p}$ together with their corresponding subgroups, studied by means of GTPack.

Mathematica

```
In[8]:= oh = GTInstallGroup[Oh, GVerbose -> False];

List of shift vectors.

In[9]:= shift = {{0, 0, 0}, {0, 0,  $\delta$ }, { $\delta$ , 0, 0}, {0,  $\delta$ , 0}, { $\delta$ ,  $\delta$ , 0}, {- $\delta$ ,  $\delta$ , 0}, { $\delta$ ,  $\delta$ /2, 0},
{ $\delta$ /2, 0,  $\delta$ }, {0,  $\delta$ /2,  $\delta$ }, { $\delta$ /2,  $\delta$ /2,  $\delta$ }, {- $\delta$ /2,  $\delta$ /2,  $\delta$ }, { $\delta$ /2,  $\delta$ /3,  $\delta$ }};

Find the symmetry groups.

In[10]:= tab = Table[0, {13}, {3}]; tab[[1]] = {"shift", "ord[G]", "G"};
Do[
  struc = str /. {pos -> {a/2, a/2, a} + shift[[k]]};  $\delta = .2$ ;
  cl = GTCluster[struc, 2, GOLattice -> {a -> 1}];
  grp = {};
  Do[
    If[GTSymmetryElementQ[oh[[i]], cl],
      grp = Append[grp, oh[[i]]],
      None
    ]
  , {i, 1, 48}];
  Clear[ $\delta$ ];
  tab[[k+1, 1]] = shift[[k]]; tab[[k+1, 2]] = GTGroupOrder[grp];
  tab[[k+1, 3]] = grp
  , {k, 1, 12}];
Grid[tab, Frame -> All, Alignment -> Center,
Dividers -> {{2 -> GTDividerColor1}, {2 -> GTDividerColor1}},
Background -> {{1 -> GTBackgroundColor1},
{1 -> GTBackgroundColor1}, {1, 1} -> GTCornerColor}, ItemSize -> Full]
```

shift	ord[G]	G
{0, 0, 0}	16	{Ee, C _{2x} , C _{2y} , C _{2b} , C _{2a} , C _{2x} , C _{4z} , IBe, IC _{2x} , IC _{2a} , IC _{2b} , IC _{2y} , IC _{2a} , IC _{4z} , IC _{4z} ² }
{0, 0, δ }	8	{Ee, C _{2x} , C _{4z} , C _{4z} ² , IC _{2x} , IC _{2a} , IC _{2b} , IC _{2y} }
{ δ , 0, 0}	4	{Ee, C _{2x} , IC _{2y} , IC _{2a} }
{0, δ , 0}	4	{Ee, C _{2y} , IC _{2x} , IC _{2a} }
{ δ , δ , 0}	4	{Ee, C _{2a} , IC _{2b} , IC _{2a} }
{- δ , δ , 0}	4	{Ee, C _{2b} , IC _{2a} , IC _{2a} }
{ δ , $\frac{\delta}{2}$, 0}	2	{Ee, IC _{2x} }
{ $\frac{\delta}{2}$, 0, δ }	2	{Ee, IC _{2y} }
{0, $\frac{\delta}{2}$, δ }	2	{Ee, IC _{2x} }
{ $\frac{\delta}{2}$, $\frac{\delta}{2}$, δ }	2	{Ee, IC _{2b} }
{- $\frac{\delta}{2}$, $\frac{\delta}{2}$, δ }	2	{Ee, IC _{2a} }
{ $\frac{\delta}{2}$, $\frac{\delta}{3}$, δ }	1	{Ee}

Figure 14.3 Symmetry groups of the low-symmetric phase in dependence on the shift of atom B.

The displacement vector $\mathbf{p}$ is a variational degree of freedom of the system. Thus, the equilibrium value $\mathbf{p}_0(T, P)$ has to be found by minimizing the GIBBS free energy $G = G(T, P, p_x, p_y, p_z)$ with respect to $\mathbf{p}$. For a second-order phase transition, the components of $\mathbf{p}$ vary continuously across T_0 . In the vicinity of T_0 , the deviations from the critical point $|T - T_0|$, $|P - P_0|$ and the displacement $|\mathbf{p}|$ are small. Therefore, G can be expressed as a series expansion with respect to $\mathbf{p}$. As will be shown in the following, the form of the series expansion is connected to the symmetry of the system. Let $\mathcal{G}$ denote the symmetry group of the high symmetry phase. Then, for all $g \in \mathcal{G}$ a given value of $\mathbf{p}$ is transformed to a vector $\mathbf{p}'$. However, the GIBBS free energy itself, $G(T, P)$, does not depend on the orientation of the system in space, i.e., $G(T, P)$ has to be invariant with respect to all transformations of $\mathcal{G}$. Up to second order terms, the series expansion can be written as

$$G(T, P) = G_0(T, P) + \sum_{i=1}^3 a_i(T, P) p_i + \sum_{i=1}^3 \sum_{j=1}^3 b_{i,j}(T, P) p_i \cdot p_j. \quad (14.1)$$

Since the transformations of $\mathcal{G}_0$ are linear, terms of different order in (14.1) do not mix. Furthermore, the quantities $a_i(T, P)$ and $b_{i,j}(T, P)$ do not depend on spatial variables and are therefore invariant under the transformations. Since the vector $\mathbf{p}$ itself is not invariant under all symmetry elements $g \in \mathcal{G}$ (in general), linear terms cannot occur within (14.1).

Furthermore, mixed terms like $x \cdot z$ cannot occur as shown in Figure 14.4. However, the elements of D_{4h} transform x^2 into y^2 and therefore $x^2 + y^2$ is invariant. Additionally, z^2 is invariant under the operations of D_{4h} . It follows that equation (14.1) can be reformulated as³⁾

$$G(T, P) = G_0(T, P) + \frac{\alpha_2(T, P)}{2} (p_x^2 + p_y^2) + \frac{\alpha_1(T, P)}{2} p_z^2. \quad (14.2)$$

Mathematica

Investigation of the mixed terms. d4hm contains symmetry elements of D_{4h} in matrix form.

```
In[8]:= f1[x_, y_, z_] := x * z; Apply[f1, Inverse[#].{x, y, z}] & /@ d4hm // Union
```

```
Out[8]:= {-x z, x z, -y z, y z}
```

Investigation of quadratic terms.

```
In[9]:= f1[x_, y_, z_] := x^2; f2[x_, y_, z_] := y^2; f3[x_, y_, z_] := z^2;
{Apply[f1, Inverse[#].{x, y, z}] & /@ d4hm // Union,
 Apply[f2, Inverse[#].{x, y, z}] & /@ d4hm // Union,
 Apply[f3, Inverse[#].{x, y, z}] & /@ d4hm // Union}
```

```
Out[10]:= {{x^2, y^2}, {x^2, y^2}, {z^2}}
```

Figure 14.4 Invariance properties of the quadratic terms within the series expansion of the GIBBS free energy.

3) Form of factors are chosen for convenience.

In the phenomenological theory the coefficients α_1 and α_2 are unrelated, i.e., no symmetry argument establishes a relationship of both coefficients as will be shown in the next section.

Per definition, for the high-temperature phase ($T > T_0$), the components of the equilibrium displacement vector $\mathbf{p}_0$ vanish. This condition is guaranteed if $\alpha_i \geq 0$ holds in (14.2). To allow for a phase transition, leading to a minimum of G for a finite $\mathbf{p}_0$, at least one of the α_i has to change sign at the phase transition temperature $T = T_0$. This requires the inclusion of higher order terms to stabilize a minimum. Similarly to first-order terms, third-order terms are excluded. Therefore, fourth-order terms have to be taken into account. Furthermore, the formulation

$$\alpha_i = \alpha_i(T, P) = \alpha_i(P_0)(T - T_0), \quad \alpha_i(P_0) > 0 \quad (14.3)$$

for the second-order parameter implements the necessary temperature dependence.

Analogously to the quadratic terms discussed in Figure 14.4, the invariance properties of quartic terms are investigated in Figure 14.5. As a result, x^4 and y^4 interchange under symmetry operations whereas z^4 remains invariant. Only $x^2 \cdot y^2$ is an invariant mixed monomial of fourth order. Finally, the following two equations describe the phase transitions

$$G = G_0 + \frac{a_1}{2}(T - T_0)p_z^2 + \frac{\beta}{4}p_z^4, \quad (14.4)$$

$$G = G_0 + \frac{a_2}{2}(T - T_0)(p_x^2 + p_y^2) + \frac{\beta_1}{4}(p_x^4 + p_y^4) + \frac{\beta_2}{2}p_x^2 \cdot p_y^2. \quad (14.5)$$

As a result the components p_z and p_x, p_y are associated with the phase transition. These are the so-called *order parameters* of the phase transition. For $\beta > 0$, the

Mathematica

Investigation of quartic terms.

```
In[8]:= f1[x_, y_, z_] := x^4; f2[x_, y_, z_] := y^4; f3[x_, y_, z_] := z^4;
{Apply[f1, Inverse[#].{x, y, z}] & /@ d4hm // Union,
 Apply[f2, Inverse[#].{x, y, z}] & /@ d4hm // Union,
 Apply[f3, Inverse[#].{x, y, z}] & /@ d4hm // Union}
```

```
Out[9]= {{x^4, y^4}, {x^4, y^4}, {z^4}}
```

Investigation of mixed quartic terms.

```
In[10]:= f1[x_, y_, z_] := x^2 y^2;
f2[x_, y_, z_] := x^2 z^2;
f3[x_, y_, z_] := x^2 y z;
{Apply[f1, Inverse[#].{x, y, z}] & /@ d4hm // Union,
 Apply[f2, Inverse[#].{x, y, z}] & /@ d4hm // Union,
 Apply[f3, Inverse[#].{x, y, z}] & /@ d4hm // Union}
```

```
Out[11]= {{x^2 y^2}, {x^2 z^2, y^2 z^2}, {-x^2 y z, x^2 y z, -x y^2 z, x y^2 z}}
```

Figure 14.5 Invariance properties of the quartic terms within the series expansion of the GIBBS free energy.

two minima of the GIBBS free energy G according to equation (14.4) are given by

$$p_{0z} = \pm \sqrt{\frac{a_1(T_0 - T)}{\beta}}. \quad (14.6)$$

As can be seen, the order parameter is twofold degenerate, corresponding to a displacement of the B -atom in $+z$ - or $-z$ -direction. Subsequently in Section 14.2, the group theoretical foundation of LANDAU's theory will be discussed more thoroughly.

14.2

Basics of the Group Theoretical Formulation

In the following, a crystal consisting of N kinds of atoms is considered. The density function $\rho_i(\mathbf{r})$ for atoms of sort i defines the probability $\rho_i(\mathbf{r})dV$ to find an atom of sort i in the volume element dV at $\mathbf{r}$. The density function $\rho(\mathbf{r})$ sums up all contributions ρ_i ,

$$\rho(\mathbf{r}) = \sum_{i=1}^N \rho_i(\mathbf{r}). \quad (14.7)$$

Furthermore, (P_0, T_0) is a point on the phase transition line with the corresponding density function $\rho_0(\mathbf{r})$. The symmetry group of $\rho_0(\mathbf{r})$ is $\mathcal{G}$. The density function is assumed to vary continuously, i.e., it can be expressed at (P, T) close to (P_0, T_0) via

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r}). \quad (14.8)$$

Since the density $\rho_0(\mathbf{r})$ is an observable quantity it captures the symmetry of the system and is transforming as the totally symmetric representation Γ^1 of $\mathcal{G}$.⁴⁾ However, $\delta\rho$ can be expanded in terms of basis functions $\phi_\mu^p(\mathbf{r})$ transforming like irreducible representations Γ^p of $\mathcal{G}$

$$\delta\rho(\mathbf{r}) = \sum_p \sum_\mu C_\mu^p \phi_\mu^p(\mathbf{r}). \quad (14.9)$$

In general, if an irreducible representation Γ^p of $\mathcal{G}$ is complex (see Section 8.7.1), the functions $\phi_\mu^p(\mathbf{r})$ are complex as well. To achieve a real valued expansion, so-called physically irreducible representations $\Gamma^p + \Gamma^{p*}$ are constructed in such a case to ensure the reality of the expansion (14.9).⁵⁾ Thus, the summation in (14.9) runs over irreducible and physically irreducible representations. The functions $\phi_\mu^p(\mathbf{r})$ depend on pressure P and temperature T . Furthermore, $\delta\rho$ is a small quantity, i.e., a series expansion of the thermodynamic potential can be used

$$G(P, T, \rho) = G(P, T, \rho_0) + G_1(P, T, \rho_0, \delta\rho) + G_2(P, T, \rho_0, \delta\rho) + \dots, \quad (14.10)$$

4) Subsequently, Γ^1 represents the totally symmetric representation of a group $\mathcal{G}$.

5) See [210, 211] for details.

where the summands G_k represent linear functionals of k th order in $\delta\rho$. Therefore:

$$G_1(P, T, \rho_0, \delta\rho) = \sum_{p, \mu} C_\mu^p G_1(P, T, \rho_0, \phi_\mu^p), \quad (14.11)$$

$$G_2(P, T, \rho_0, \delta\rho) = \sum_{p, \mu} \sum_{p', \mu'} C_\mu^p C_{\mu'}^{p'} G_2(P, T, \rho_0, \phi_\mu^p, \phi_{\mu'}^{p'}). \quad (14.12)$$

The thermodynamic potential G is invariant under rotations of the coordinate system. In general, a transformation by an element $T \in \mathcal{G}$ transforms the basis functions ϕ_μ^p . Since the ϕ_μ^p form a basis of a subspace, a transformation of G_k can also be expressed as a transformation of the coefficients instead of a transformation of the functions. That means the coefficients are transformed with respect to irreducible representations of $\mathcal{G}$. However, since the potential has to be invariant, it can only depend on invariant combinations of the C_μ^p . In (14.11) only the coefficient C_1^1 corresponds to the totally symmetric representation of $\mathcal{G}$ and is invariant, i.e.,

$$G_1(P, T, \delta\rho) = C_1^1 G_1(P, T, \rho, \phi_1^1). \quad (14.13)$$

Corresponding to the form of invariants of degree 2, G_2 has the form

$$G_2(P, T, \delta\rho) = \sum_p A^p(P, T) \sum_\mu |C_\mu^p|^2. \quad (14.14)$$

To ensure that (P_0, T_0) is on the phase transition line at least one of the coefficients A^p has to be zero at (P_0, T_0) ,

$$A^{\bar{p}}(P_0, T_0) = 0. \quad (14.15)$$

$A^{\bar{p}}$ changes sign at (P_0, T_0) , whereas the other A^p are positive. On the side $A^{\bar{p}} > 0$, i.e., $C_\mu^p = 0$, $p \neq 1$ the density has the same symmetry as ρ_0 . On the other side of the phase transition line, the density is given by

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \sum_\mu C_\mu^{\bar{p}} \phi_\mu^{\bar{p}}(\mathbf{r}). \quad (14.16)$$

The symmetry group $\mathcal{G}'$ after the phase transition is a subgroup of $\mathcal{G}$ consisting of those elements of $\mathcal{G}$ leaving $\rho(\mathbf{r})$ in (14.16) invariant. To find $\mathcal{G}'$ it is necessary to know the $C_\mu^{\bar{p}}$. Not all irreducible representations of $\mathcal{G}$ lead to a lowering of symmetry in a phase transition of second order. To have this property an irreducible representation has to fulfill two criteria. If it does so, it is called active.⁶⁾

- LANDAU criterion

Invariants of degree 3 build from the $C_\mu^{\bar{p}}$ are forbidden in the expansion of the

6) For details to the criteria see again [210, 211].

thermodynamic potential G . In terms of representation theory it is formulated as

$$\Gamma^1 \not\subset [\Gamma^{\bar{p}}]^3, \quad (14.17)$$

i.e., the symmetrized third power of the irreducible representation under consideration must not contain Γ^1 .

- LIFSHITZ criterion

The LIFSHITZ criterion considers space groups and is given by

$$\Gamma^1 \not\subset \Gamma^{\text{vec}} \otimes \left\{ \Gamma^{\bar{p}}(\mathbf{k}_0) \right\}^2, \quad (14.18)$$

where $\mathbf{k}_0$ reflects the $\mathbf{k}$ -dependence of irreducible representations of space groups. It states that the product of the vector representation and the antisymmetric second power of the corresponding irreducible representation must not contain Γ^1 . Since the irreducible representations of space groups are labeled by a combined index $(i, \mathbf{k})$, a discrete sum over i and a BRILLOUIN zone integration appears within the decomposition. However, it turns out that only high symmetry points of the BRILLOUIN zone have to be considered. The criterion ensures that the invariance groups of possible low symmetry phases are space groups as well.

14.3

Examples with GTPack Commands

14.3.1

Invariant Polynomials

Within the construction of the thermodynamic potential invariant combinations of the coefficients C_μ^p of an irreducible representation Γ^p of $\mathcal{G}$ have to be found. This is closely connected to the problem of constructing invariant polynomials.

Polynomials, invariant under all operations of the corresponding symmetry group, are called *invariant* polynomials. They transform as the identity representation Γ^1 . **GTSymmetryBasisFunctions** can be used to construct such polynomials. For the example of point group C_{3v} , the method is demonstrated for polynomials of order up to 4.⁷⁾ The polynomials are constructed from monomials of the corresponding orders. Constant factors are not significant here. The *Mathematica* command **MonomialList** is used to create the list of monomials from $(x + y)^p$. The resulting polynomials are revealed in Figure 14.6. In the case of $p = 1$ x , y are basis functions of the representation Γ^3 of C_{3v} . A linear combination of x and y does not lead to a totally symmetric function with respect to the operations of C_{3v} . The invariant polynomial for $p = 2$ is $(x^2 + y^2)$. For $p = 3$ and $p = 4$ the invariant polynomials $x(x^2 - 3y^2)$ and $(x^2 + y^2)^2$ are found.

7) See TOLEDANO [210], p. 33f for more information.

Mathematica

Character table of point group C_{3v}

```
In[8]:= c3vct = GTCharacterTable[c3v];
```

	Ee	$2 C_{3z}$	$3 IC_{2D}$
Γ^1	1	1	1
Γ^2	1	1	-1
Γ^3	2	-1	0

$C_1 = \{Ee\}$

$C_2 = \{C_{3z}, C_{3z}\}$

$C_3 = \{IC_{2D}, IC_{2C}, IC_{2y}\}$

Monomial list up to order 4.

```
In[9]:= mlist = Table[MonomialList[(x + y)^p] // Expand, {p, 1, 4}]
```

```
Out[9]:= {{x, y}, {x^2, 2 x y, y^2}, {x^3, 3 x^2 y, 3 x y^2, y^3}, {x^4, 4 x^3 y, 6 x^2 y^2, 4 x y^3, y^4}}
```

Construction of invariant polynomials.

```
In[10]:= Table[GTSymmetryBasisFunctions[c3vct, mlist[[i]]], {i, 1, 4}];
```

	Γ^1	Γ^2	Γ^3
x	0	0	x
y	0	0	y

	Γ^1	Γ^2	Γ^3
x^2	$\frac{1}{2} (x^2 + y^2)$	0	$\frac{1}{2} (x^2 - y^2)$
$2 x y$	0	0	$2 x y$
y^2	$\frac{1}{2} (x^2 + y^2)$	0	$\frac{1}{2} (-x^2 + y^2)$

	Γ^1	Γ^2	Γ^3
x^3	$\frac{1}{4} (x^3 - 3 x y^2)$	0	$\frac{3}{4} x (x^2 + y^2)$
$3 x^2 y$	0	$\frac{3}{4} (3 x^2 y - y^3)$	$\frac{3}{4} y (x^2 + y^2)$
$3 x y^2$	$-\frac{3}{4} (x^3 - 3 x y^2)$	0	$\frac{3}{4} x (x^2 + y^2)$
y^3	0	$\frac{1}{4} (-3 x^2 y + y^3)$	$\frac{3}{4} y (x^2 + y^2)$

	Γ^1	Γ^2	Γ^3
x^4	$\frac{3}{8} (x^2 + y^2)^2$	0	$\frac{1}{8} (5 x^4 - 6 x^2 y^2 - 3 y^4)$
$4 x^3 y$	0	0	$4 x^3 y$
$6 x^2 y^2$	$\frac{3}{4} (x^2 + y^2)^2$	0	$-\frac{3}{4} (x^4 - 6 x^2 y^2 + y^4)$
$4 x y^3$	0	0	$4 x y^3$
y^4	$\frac{3}{8} (x^2 + y^2)^2$	0	$\frac{1}{8} (-3 x^4 - 6 x^2 y^2 + 5 y^4)$

Figure 14.6 Construction invariant polynomials of C_{3v} up to degree $p = 4$.

14.3.2

LANDAU and LIFSHITZ Criterion

The LANDAU and the LIFSHITZ criterion discuss the antisymmetrized third power and the symmetrized second power of a representation (cf. Section 14.2). It can be evaluated directly from the characters of the representations. Table 14.1 shows the symmetrized powers of a representation. The general method described by LJUBARSKI [211] is implemented in **GTSymmetrizedProductChars**. With that, the

Table 14.1 Characters of symmetrized powers of a representation.

Representation	Character
$[I]^2$	$\frac{1}{2} (\chi(g^2) + \chi^2(g))$
$[I]^3$	$\frac{1}{3}\chi(g^3) + \frac{1}{2}\chi^2(g)\chi(g) + \frac{1}{6}\chi^3(g)$
$[I]^4$	$\frac{1}{4}\chi(g^4) + \frac{1}{3}\chi(g^3)\chi(g) + \frac{1}{8}\chi^2(g^2) + \frac{1}{4}\chi(g^2)\chi^2(g) + \frac{1}{24}\chi^4(g)$

calculation of the characters of the symmetrized and antisymmetrized product of arbitrary order is possible.

Example 66 (The LANDAU criterion for the group $C_{3\nu}$). As an example, the characters of the symmetrized second and third power of the two-dimensional ir-reducible representation of $C_{3\nu}$ are calculated using **GTSymmetrizedProductChars** (see Figure 14.7). The considered representations are three- and four-dimensional, i.e., reducible with respect to $C_{3\nu}$. The reduction reveals that $[I^3]^2$ is a direct sum

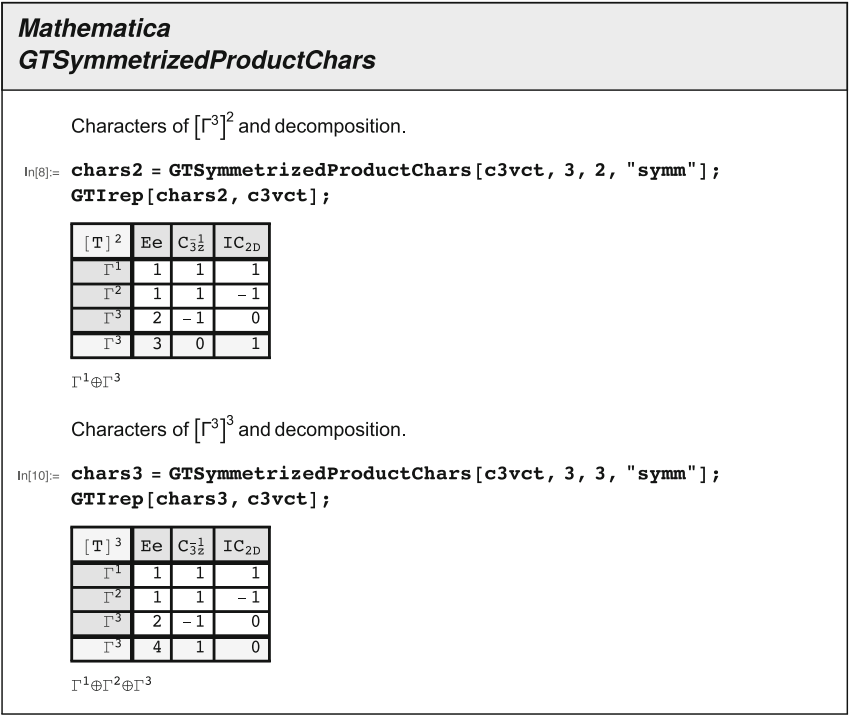


Figure 14.7 Characters of symmetrized and antisymmetrized powers of a representation (c3vct contains the charcter table of the point group $C_{3\nu}$).

of Γ^1 and Γ^3 . The functions that belong to the two subspaces of $[\Gamma^3]^2$ are discussed in Figure 14.6. $[\Gamma^3]^3$ also contains the representation Γ^2 . The corresponding basis functions of $[\Gamma^3]^3$ can be found in Figure 14.6,

$$\Gamma^1: x(x^2 - 3y^2), \quad \Gamma^2: y(3x^2 - y^2), \quad \Gamma^3: x(x^2 + y^2), y(x^2 + y^2). \quad (14.19)$$

Example 67 (The LIFSHITZ criterion for the group D_4). The LIFSHITZ criterion will be evaluated at the Γ point of the BRILLOUIN zone, where the discussion of the irreducible representations of the space group reduces to the investigation of the corresponding point group. The point group is assumed to be D_4 . Furthermore, the two-dimensional representation Γ^5 is studied (see Figure 14.8). The vector

Mathematica

Installation of D_4 , construction of character table.

```
In[8]:= d4 = GTInstallGroup[D4, GOverbose -> False];
d4ct = {classes, chars, names} = GTCharacterTable[d4];
```

	Ee	2 C _{2z}	2 C _{2d}	2 C _{4y}	C _{2y}
Γ^1	1	1	1	1	1
Γ^2	1	-1	-1	1	1
Γ^3	1	-1	1	-1	1
Γ^4	1	1	-1	-1	1
Γ^5	2	0	0	0	-2

$C_1 = \{Ee\}$

$C_2 = \{C_{2z}, C_{2x}\}$

$C_3 = \{C_{2d}, C_{2c}\}$

$C_4 = \{C_{4y}, C_{4y}^{-1}\}$

$C_5 = \{C_{2y}\}$

Vector representation.

```
In[10]:= vrep = GTVectorRep[d4ct, GOverbose -> True];
```

$\Gamma^2 \oplus \Gamma^5$

Characters of $\{\Gamma^5\}^2$ of the two-dimensional irreducible representation.

```
In[11]:= asymm = GTSymmetrizedProductChars[d4ct, 5, 2, "asymm", GOverbose -> False]
```

```
Out[11]= {1, -1, -1, 1, 1}
```

Characters of $\Gamma^{\text{vec}} \times \{\Gamma^5\}^2$

```
In[12]:= dpc = GTDirectProductChars[chars[[2]], asymm] +
GTDirectProductChars[chars[[5]], asymm]
```

```
Out[12]= {3, 1, 1, 1, -1}
```

Decomposition

```
In[13]:= GTIrep[dpc, d4ct];
```

$\Gamma^1 \oplus \Gamma^5$

Figure 14.8 Example for the investigation of the LIFSHITZ criterion.

representation Γ^{vec} and the second antisymmetric power of Γ^5 enter the LIFSHITZ criterion. The maximum dimension of irreducible representations of D_4 is two, i.e., the vector representation is a direct sum of Γ^2 and Γ^5 . The characters of $\{\Gamma^5\}^2$ are found by means of **GTSymmetrizedProductChars**. The characters of the direct products of the irreducible parts of Γ^{vec} and $\{\Gamma^5\}^2$ are calculated using **GTDirectProductChars** and summed up. Finally, the direct product is decomposed into irreducible representations of D_4 . The direct sum contains Γ^1 , i.e., the LIFSHITZ condition is not fulfilled. However, the LANDAU condition is fulfilled. Nevertheless, the representation is passive all together.

Appendix A

Spherical Harmonics

The spherical harmonics are the solution of the eigenvalue equation

$$\left[\frac{1}{\sin(\vartheta)} \frac{\partial}{\partial \vartheta} \left(\sin(\vartheta) \frac{\partial}{\partial \vartheta} \right) + \frac{1}{\sin^2(\vartheta)} \frac{\partial^2}{\partial \varphi^2} \right] Y_l^m(\vartheta, \varphi) = -l(l+1) Y_l^m(\vartheta, \varphi). \quad (\text{A.1})$$

The differential operator on the left-hand side of (A.1) occurs as the angular part of the LAPLACE operator. The spherical harmonics $Y_l^m(\vartheta, \varphi)$ can be defined in multiple ways, two of those (the complex spherical harmonics and the real tesseral harmonics) are explained in the following.

For the solution of (A.1), the spherical harmonics can be found by the ansatz $Y_l^m(\vartheta, \varphi) = \Theta(\vartheta)\Phi(\varphi)$ [224], which leads to

$$\sin^2(\vartheta) \left[\frac{1}{\Theta(\vartheta)\sin(\vartheta)} \frac{\partial}{\partial \vartheta} \left(\sin(\vartheta) \frac{\partial \Theta(\vartheta)}{\partial \vartheta} \right) + l(l+1) \right] = -\frac{1}{\Phi(\varphi)} \frac{\partial^2 \Phi(\varphi)}{\partial \varphi^2}. \quad (\text{A.2})$$

By defining the separation constant by m^2 , the polar equation and the azimuthal equation can be obtained, as

$$\frac{1}{\sin(\vartheta)} \frac{\partial}{\partial \vartheta} \left(\sin(\vartheta) \frac{\partial \Theta(\vartheta)}{\partial \vartheta} \right) + l(l+1)\Theta(\vartheta) - \frac{m^2}{\sin^2(\vartheta)}\Theta(\vartheta) = 0 \quad (\text{A.3})$$

and

$$\frac{\partial^2 \Phi(\varphi)}{\partial \varphi^2} + m^2 \Phi(\varphi) = 0. \quad (\text{A.4})$$

The solution of the polar equation is given by the associated LEGENDRE polynomials P_l^m ,

$$\Theta(\vartheta)_l^m = \sqrt{\frac{2l+1}{2} \cdot \frac{(l-m)!}{(l+m)!}} \cdot P_l^m[\cos(\vartheta)]. \quad (\text{A.5})$$

The choice to construct the solution of the azimuthal equation to be either complex or real, leads to the definition of the complex spherical harmonics and the real tesseral harmonics.

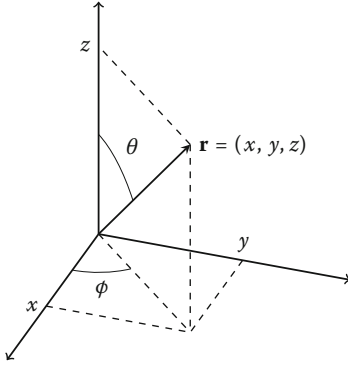


Figure A.1 Spherical coordinate system.

A.1

Complex Spherical Harmonics

A.1.1

Definition of Complex Spherical Harmonics

For the definition of the complex spherical harmonics, the following solution of the azimuthal equation (A.4) is chosen,

$$\Phi(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}. \quad (\text{A.6})$$

The prefactor $1/\sqrt{2\pi}$ is used to satisfy the normalization $\int_0^{2\pi} d\varphi |\Phi(\varphi)|^2 = 1$. Hence, the complex spherical harmonics are given by

$$Y_l^m(\vartheta, \varphi) = N_l^m P_l^m[\cos(\vartheta)] e^{im\varphi}, \quad (\text{A.7})$$

where N_l^m is the normalization factor

$$N_l^m = \sqrt{\frac{2l+1}{4\pi} \cdot \frac{(l-m)!}{(l+m)!}}. \quad (\text{A.8})$$

The spherical harmonics are implemented in *Mathematica* and can be obtained by using the command **SphericalHarmonicY**.

A.1.2

Cartesian Spherical Harmonics

In some cases, it is useful to express the spherical harmonics in Cartesian coordinates. In comparison to the definition of the spherical coordinate system, the following expressions can be derived,

$$\sin(\varphi) = \frac{y}{\sqrt{x^2 + y^2}}, \quad \cos(\varphi) = \frac{x}{\sqrt{x^2 + y^2}}, \quad (\text{A.9})$$

and

$$\cos(\vartheta) = \frac{z}{\sqrt{x^2 + y^2 + z^2}}. \quad (\text{A.10})$$

Since m can be positive and negative, EULER's identity has to be written in an inappropriate way,

$$e^{im\varphi} = \cos|m|\varphi + i \operatorname{sign}(m) \sin|m|\varphi. \quad (\text{A.11})$$

Now the following trigonometric identities can be used,

$$\sin(|m|\varphi) = \sum_{k=0}^{\infty} \binom{|m|}{k} \cos^k(\varphi) \sin^{|m|-k}(\varphi) \sin\left(\frac{|m|-k}{2} \cdot \pi\right) \quad (\text{A.12})$$

and

$$\cos(|m|\varphi) = \sum_{k=0}^{\infty} \binom{|m|}{k} \cos^k(\varphi) \sin^{|m|-k}(\varphi) \cos\left(\frac{|m|-k}{2} \cdot \pi\right). \quad (\text{A.13})$$

Putting everything together and using the abbreviation $r = \sqrt{x^2 + y^2 + z^2}$ one finally ends up with an equation for the spherical harmonics in Cartesian form,

$$\begin{aligned} Y_l^m(x, y, z) &= N_l^m P_l^m\left(\frac{z}{r}\right) \sum_{k=0}^{\infty} \binom{|m|}{k} \frac{x^k y^{|m|-k}}{(x^2 + y^2)^{|m|}} \\ &\quad \times \left[\cos\left(\frac{|m|-k}{2} \cdot \pi\right) + i \operatorname{sign}(m) \sin\left(\frac{|m|-k}{2} \cdot \pi\right) \right]. \end{aligned} \quad (\text{A.14})$$

GTPack provides the Cartesian spherical harmonics by the command **GTCartesianSphericalHarmonicY**.

A.1.3

Transformation Behavior of Complex Spherical Harmonics

The spherical harmonics form the basis of a HILBERT space, and furthermore $Y_l^{-l}, Y_l^{-l+1}, \dots, Y_l^{l-1}, Y_l^l$ is a basis of a $2l + 1$ -dimensional subspace. Hence, any rotation of the coordinate system applied to a function Y_l^m can be evaluated into the basis of the subspace as

$$\hat{P}(T)Y_l^m = \sum_{m'=-l}^l Y_l^{m'} D_{m'm}^l(T). \quad (\text{A.15})$$

Here, the matrix $D_{m'm}^l(T)$ is called the WIGNER D-function or the WIGNER D-matrix. For proper rotations, the WIGNER D-matrix is implemented in *Mathematica* as **WignerD**. For improper rotations, a factor $(-1)^l$ has to be multiplied.

Furthermore, $D_{m'm}^l(T)$ is a representation matrix of the element T . Within **GT-Pack** it is possible to install the matrix representation $D_{m'm}^l(T)$ for all $T \in \mathcal{G}$ using **GTAngularMomentumRep**. If only the character system is needed, one can use **GTAngularMomentumChars**. The obtained representation is denoted by D^l . D^l is reducible in general.

If one writes equation (A.15) in matrix form ($\mathbf{Y}_l$ is defined as a row vector), one can verify the application of the character projection operator of a certain group $\mathcal{G}$ and an irreducible representation Γ^p of $\mathcal{G}$ as follows

$$\hat{\mathcal{P}}^p \mathbf{Y}_l = \frac{l_p}{g} \sum_{T \in \mathcal{G}} \chi^p(T) \mathbf{Y}_l \cdot \underline{\mathbf{D}}^l(T). \quad (\text{A.16})$$

The application of the character projection operator to spherical harmonics in algebraic form is implemented in **GT-Pack**, using **GTWignerCharProjectionOperator**. Analogously, the application of the ordinary projection operator

$$\hat{\mathcal{P}}_{ij}^p \mathbf{Y}_l = \frac{l_p}{g} \sum_{T \in \mathcal{G}} \Gamma_{ij}^p(T) \mathbf{Y}_l \cdot \underline{\mathbf{D}}^l(T). \quad (\text{A.17})$$

can be performed using **GTWignerProjectionOperator**.

A.2

Tesseral Harmonics

A.2.1

Definition of Tesseral Harmonics

In contrast to the complex valued solution of the azimuthal equation (A.4), one can use real-valued solutions given by the sine and cosine functions. **GT-Pack** uses the definition analogously to **PODOLSKIY** and **VOGL** [125], which is given by

$$S_l^m(\vartheta, \varphi) = \begin{cases} \sqrt{2}(-1)^m \Re [Y_l^m(\vartheta, \varphi)] & m > 0 \\ Y_l^0(\vartheta, \varphi) & m = 0 \\ \sqrt{2}(-1)^m \Im [Y_l^{-m}(\vartheta, \varphi)] & m < 0 \end{cases}. \quad (\text{A.18})$$

To better distinguish tesseral harmonics and complex spherical harmonics, the notation S_l^m is used for tesseral harmonics. Since the real and imaginary part of the spherical harmonics can be expressed by $\Re Y_l^m = \frac{1}{2}(Y_l^m + Y_l^{m*})$ and $\Im Y_l^m = \frac{1}{2i}(Y_l^m - Y_l^{m*})$ and furthermore $Y_l^{m*} = (-1)^m Y_l^{-m}$, the tesseral harmonics can be expressed by

$$S_l^m(\vartheta, \varphi) = \sum_{m'=-l}^l Y_l^{m'} a_{m'm}^l \quad \text{or} \quad \mathbf{S}_l = \mathbf{Y}_l \cdot \underline{\mathbf{a}}^l, \quad (\text{A.19})$$

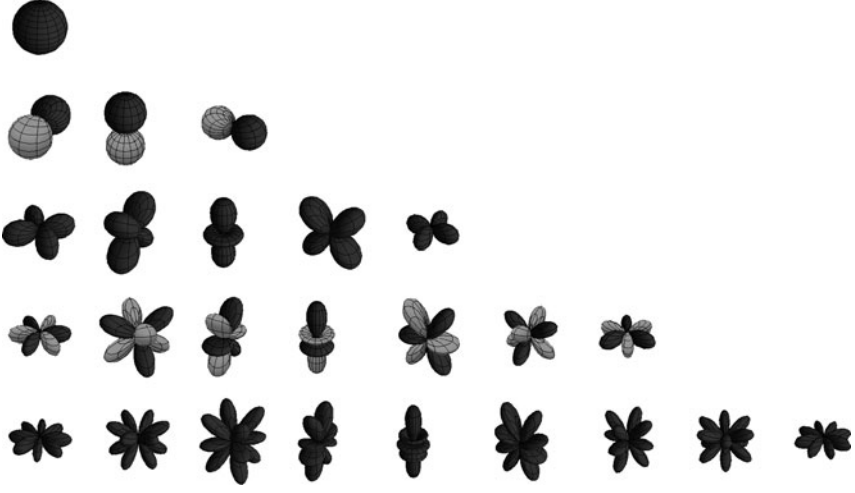


Figure A.2 Tesseral harmonics plotted from top $l = 0$ to bottom $l = 4$ and from left $m = -l$ to right $m = l$ using `GTesseralHarmonicY` and `SphericalPlot3D`.

using the $(2l + 1) \times (2l + 1)$ -dimensional square matrix $\underline{a}^l$ with entries

$$a_{m'm}^l = \begin{cases} \frac{1}{\sqrt{2}} \left((-1)^m \delta_{m'm} + \delta_{(-m')m} \right) & m > 0 \\ \delta_{m'm} & m = 0 \\ \frac{1}{\sqrt{2}i} \left((-1)^m \delta_{(-m')m} - \delta_{m'm} \right) & m < 0 \end{cases} . \quad (\text{A.20})$$

The tesseral harmonics are usually used in quantum mechanics and agree with the physicists picture of dumbbell-shaped p -orbitals (see figure A.2).

A.2.2

Cartesian Tesseral Harmonics

Since the spherical harmonics are given by $Y_l^m(\vartheta, \varphi) = \Theta_l^m(\vartheta)\Phi_l^m(\varphi)$, where $\Theta_l^m(\vartheta)$ is real and $\Phi_l^m(\varphi) = \sqrt{2}e^{im\varphi}$ is complex valued, the real and imaginary part of the spherical harmonics can be expressed by

$$\Re [Y_l^m(\vartheta, \varphi)] = N_l^m P_l^m(\cos(\vartheta)) \cos(m\varphi) \quad (\text{A.21})$$

and

$$\Im [Y_l^m(\vartheta, \varphi)] = N_l^m P_l^m(\cos(\vartheta)) \sin(m\varphi) . \quad (\text{A.22})$$

Analogously to the discussion for Cartesian spherical harmonics in the previous section, $\cos(\vartheta)$, $\sin(m\varphi)$ and $\cos(m\varphi)$ can be substituted by polynomials in x , y and z (compare the equations (A.9) and (A.10)). Using the abbreviations

$r = \sqrt{x^2 + y^2 + z^2}$ and $B_k^m(x, y) = \binom{m}{k} \frac{x^k y^{m-k}}{(x^2 + y^2)^m}$, the following expression can be found for the Cartesian tesseral harmonics,

$$S_l^m(x, y, z) = \begin{cases} \sqrt{2}(-1)^m N_l^m P_l^m \left[\frac{z}{r} \right] \sum_{k=0}^{\infty} B_k^m(x, y) \cos \left(\frac{m-k}{2} \cdot \pi \right) & m > 0 \\ N_l^0 P_l^0 \left[\frac{z}{r} \right] & m = 0 \\ \sqrt{2}(-1)^m N_l^{|m|} P_l^{|m|} \left[\frac{z}{r} \right] \sum_{k=0}^{\infty} B_k^{|m|}(x, y) \sin \left(\frac{|m|-k}{2} \cdot \pi \right) & m < 0 \end{cases} \quad (\text{A.23})$$

Cartesian tesseral harmonics are implemented within GTPack and can be given by means of the command **GTCartesianTesseralHarmonicY**.

A.2.3

Transformation Behavior of Tesseral Harmonics

Analogously to the transformation of complex spherical harmonics, the matrix $\underline{\underline{E}}^l$ can be defined, which describes the transformation of tesseral harmonics S_l^m by

$$\hat{P}(T) S_l^m(\vartheta, \varphi) = \sum_{m'=-l}^l S_l^{m'}(\vartheta, \varphi) E_{m'm}^l(T), \quad (\text{A.24})$$

or in matrix form

$$\hat{P}(T) \mathbf{S}_l(\vartheta, \varphi) = \mathbf{S}_l(\vartheta, \varphi) \underline{\underline{E}}^l(T). \quad (\text{A.25})$$

In the following, the relationship between the matrix $\underline{\underline{E}}^l$ and the WIGNER D-matrix $\underline{\underline{D}}^l$ is investigated. Since $S_l^m(\vartheta, \varphi)$ can be expressed as a linear combination of $Y_l^m(\vartheta, \varphi)$, it is possible to write

$$\hat{P}(T) \mathbf{S}_l(\vartheta, \varphi) = \hat{P}(T) \mathbf{Y}_l(\vartheta, \varphi) \cdot \underline{\underline{a}}^l \quad (\text{A.26})$$

$$= \mathbf{Y}_l(\vartheta, \varphi) \cdot \underline{\underline{D}}^l(T) \cdot \underline{\underline{a}}^l. \quad (\text{A.27})$$

However, since $\mathbf{Y}_l = \mathbf{S}_l \cdot (\underline{\underline{a}}^l)^{-1}$, one obtains

$$\hat{P}(T) \mathbf{S}_l(\vartheta, \varphi) = \mathbf{S}_l \cdot \left[(\underline{\underline{a}}^l)^{-1} \cdot \underline{\underline{D}}^l(T) \cdot \underline{\underline{a}}^l \right]. \quad (\text{A.28})$$

Hence, the transformation matrix $\underline{\underline{E}}^l(T)$ can be expressed in terms of the transformation matrix $\underline{\underline{D}}^l(T)$ via a similarity transformation

$$\underline{\underline{E}}^l(T) = (\underline{\underline{a}}^l)^{-1} \cdot \underline{\underline{D}}^l(T) \cdot \underline{\underline{a}}^l. \quad (\text{A.29})$$

Like the WIGNER D-matrices, the matrices $\underline{\underline{E}}^l(T)$ form a matrix representation of a group $\mathcal{G}$ containing the element T . Within GTPack they can be installed using **GTWignerProjectionOperator** and specifying the option **GOHarmonics**→“Real”. Since the characters are invariant under similarity transformations, the traces of $\underline{\underline{E}}^l(T)$ and $\underline{\underline{D}}^l(T)$ have to be the same,

$$\text{Tr } \underline{\underline{E}}^l(T) = \text{Tr } \underline{\underline{D}}^l(T). \quad (\text{A.30})$$

Appendix B

Remarks on Databases

For many fields of application it is reasonable to incorporate databases into the GTPack framework. Such data sets are databases for crystal or molecular structures as well as databases containing parameters for tight-binding Hamiltonians, pseudopotentials, or crystal field theory. In connection to the particular application, commands are provided to store, change, or retrieve data. Subsequently some databases provided by GTPack are introduced.

B.1

Electronic Structure Databases

B.1.1

Tight-Binding Calculations

The content of a tight-binding database can be displayed by means of **GTTb-DatabaseInfo**. Next to the stored parameters, the table also displays literature references to allow for a comparison of band structures calculated by means of GTPack and the original ones. If the description of a parameter set contains (R) at the end of the reference section, a recalculation of the parameters from the original source is performed, as explained below.

Most of the tight-binding parameter sets are given in the orthogonal two-center approximation. The database `TB_Handbook.parm` is a standard database provided by GTPack, containing a collection of sets for elemental solids with fcc, bcc, and hcp structure from [144, 145]¹⁾. `TB_Handbook.parm` does not provide information about spin–orbit coupling.

Some parameter sets in the nonorthogonal two-center approximation from [145] and other sources are provided in `TB_Nonorthogonal_H.parm` and `TB_Nonorthogonal_S.parm`. The first contains the parameters for the Hamiltonian and the latter the parameters for the overlap matrix.

1) [144, 145] also contain parameters in two-center nonorthogonal and three-center approximations.

Database `TB_Semiconductors.parm` contains parameter sets of elemental and compound semiconductors in orthogonal two-center representation using the standard SLATER–KOSTER nomenclature [126]. Some references use a different nomenclature. A recalculation has been performed using the following formulas derived from [225] for the datasets in [156, 225].

$$(ss\sigma) = \frac{1}{4} V(s, s) \quad (\text{B.1})$$

$$(ps\sigma) = \frac{\sqrt{3}}{4} V(pa, sc), \quad (sp\sigma) = \frac{\sqrt{3}}{4} V(sa, pc) \quad (\text{B.2})$$

$$(pp\sigma) = \frac{1}{4} [V(x, x) + 2V(x, y)] \quad (\text{B.3})$$

$$(pp\pi) = \frac{1}{4} [V(x, x) - V(x, y)] \quad (\text{B.4})$$

$V(sa, pc)$ denotes the interaction of an anion s -orbital with a cation p -orbital.

`TB_Oxides.parm` contains some orthogonal two-center parameter sets of monoxides and more complex oxides like BaTiO_3 .

Finally, `TB_Selected_Systems.parm` contains auxiliary parameter sets. Again, the parameter sets are in orthogonal two-center form. Some sets are recalculated from an orthogonal three-center form, indicated by (R) at the end of the reference section. The formulas in the paper of SLATER and KOSTER [126] or the command **GTTbMatrixElement** can be used to get a system of equations for this recalculation. In general, this transformation is not bijective.

B.1.2

Pseudopotential Calculations

The database `PseudoPot.parm` contains data to calculate the electronic structure of semiconductors in the framework of empirical pseudopotential theory. The information about the pseudopotentials is provided either directly by means of a set of pseudopotential coefficients or via parameters of model potentials.

The pseudopotential coefficients are mainly taken from [142] and [226]. The coefficients are usually given in symmetrized form. In the database, the data is stored as coefficients for the cation $V_C(\mathbf{G})$ and the anion $V_A(\mathbf{G})$. The following equations define the relations between the symmetrized form ($V^S(\mathbf{G})$, $V^{AS}(\mathbf{G})$) and the form used,

$$V_C(\mathbf{G}) = \frac{V^S(\mathbf{G}) + V^{AS}(\mathbf{G})}{2}, \quad V_A(\mathbf{G}) = \frac{V^{AS}(\mathbf{G}) - V^S(\mathbf{G})}{2} \quad (\text{B.5})$$

The cation is placed at $\mathbf{r}_C = (0, 0, 0)a$ and the anion at $\mathbf{r}_A = (1/4, 1/4, 1/4)a$ in the corresponding structure file of the zinc-blende structure.

Parameters for model potentials are taken mainly from [139–141]. The potentials are defined as empty-core potentials. It is possible to include bond charges.

B.1.3

Radial Integrals for Crystal Field Parameters

The database `CFDatabase.parm` contains numerical values of calculated radial integrals necessary for constructing crystal field Hamiltonians as explained in Sections 7.4.2 and 7.4.3 and particularly in Example 42. The parameters were calculated in the framework of density functional theory [105, 106] including the so-called self-interaction correction [227] to the exchange correlation functional as published in [114].

B.2

Molecular Databases

The database `Molecules.parm` for molecules contains data to discuss the vibrational properties in terms of group theory. *Mathematica* itself provides a large amount of information about molecules. As an interface, the command **GTMolChemicalData** allows one to extract information useful in group theoretical considerations from the *Mathematica* database and to transform it into a special GTPack format. The command **GTMolToCluster** extracts the structural information of a molecular data set in a form used for clusters of atoms. Such a transformation allows one to apply other GTPack commands, e.g., for the construction of a real-space tight-binding model.

B.3

Database of Structures

A basic structural database `GTPack.struc` is provided by GTPack, containing structures related to examples and tasks used throughout this book. The database itself can be extended using the command **GTInstallStructure**. GTPack also contains interfaces to major crystal structure databases such as the *Crystallography Open Database* [46]. There, the structural data is stored in the CIF format and can be imported using **GTImportCIF**.

Appendix C

Use of MPB together with GTPack

The MIT Photonic Bands (MPB) package represents a well-established photonic-band structure code. Details about the implementation can be found in [174, 175]. The output of MPB can be imported by GTPack for further analysis. However, some transformation of the output of an MPB calculation is necessary for that. Typically, MPB is executed via

$$\text{mpb} < \text{problem.ctf} > \text{problem.out} , \quad (\text{C.1})$$

where the control file `problem.ctf` contains all input parameters and the output is stored in `problem.out`. The output has to be filtered with respect to the planned use of the data in GTPack. A subdirectory in the GTPack distribution contains `#.ctf` files for problems discussed in Chapters 11 and 12.¹⁾

C.1

Calculation of Band Structure and Density of States

Within the output data of MPB is a part containing the results of the band structure calculation. This part starts with special tokens like `tmfreqs`, `tefreqs`, or `freqs` for two-dimensional calculations with TM or TE polarization or three-dimensional calculations, respectively. The script **GSMPBBands2D**²⁾ is used to extract the band structure information applicable for GTPack. If a two-dimensional calculation for TM and TE polarization was performed

$$\text{GSMPBBands2D} \quad \text{problem.out} \quad (\text{C.2})$$

results in the two files `bands2d_TM` and `bands2d_TE`. The files can be imported using **GTPhMPBBands**. The script **GSMPBBands3D** works similarly for three-dimensional calculations producing a file `bands3D`. **GTBandsPlot** can be used to plot the imported band structures.

- 1) The directory is located in the documentation path:
Documentation/English/ReferencePages/Symbols/datasets/MPB.
- 2) All scripts belonging to GTPack start with GS. They can be found in a special directory for scripts within the GTPack distribution.

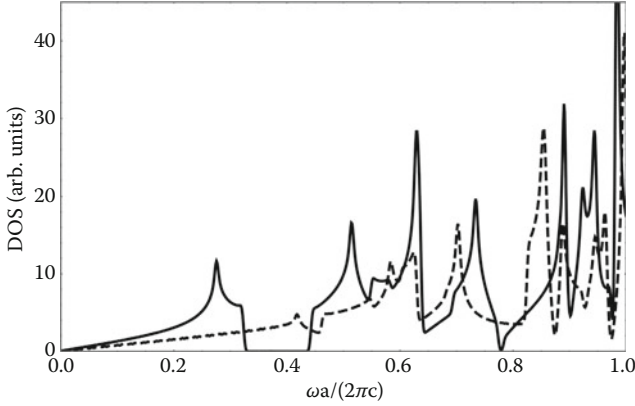


Figure C.1 Density of states for dielectric rods in air ($r = 0.2a$, $\epsilon = 8.9$). Bands are calculated by means of MPB, DOS is calculated with GTPack. TE modes – dashed line, TM modes – solid line.

As explained in Chapters 11 and 12, photonic band structures and density of states can be calculated using GTPack. However, for large eigenvalue problems, MPB might be the more appropriate tool. The $\mathbf{k}$ -mesh for photonic band structure calculations can be generated using **GTBZPointMesh** and exported into a form used in the control file of MPB by applying **GTBZMPBPointMesh**. For density of states calculations, the commands **GTDensityOfStates** and **GTDensityOfStatesPlot** can be used. For example, the density of states can be calculated within GTPack by incorporating a band structure calculated using MPB as shown in Figure C.1. The corresponding band structure calculation itself by means of GTPack was discussed in Figure 11.4.

C.2

Calculation of Eigenmodes

The symmetry analysis of band structures is based on the eigenmodes. Eigenmodes calculated using MPB can be imported into GTPack. After the calculation of the eigenmodes at the high symmetry points (check [175] for detailed information) it is necessary to use the program `mpb-data` to recast the data to a rectangular cell, to set the resolution accordingly and to eventually prepare multiple unit cells for the plot. Typically, this is done using the following shell command

$$\text{mpb-data -r -m 3 -n 32 epsilon.h5.} \quad (\text{C.3})$$

The file of the permittivity distribution in real space is used as an example. The output consists of a rectangular cell. The resolution is set to 32 grid points per lattice constant and 3 unit cells are plotted in each direction. It is important to note that the hdf5-file contains the recalculated data as new data sets. After this

treatment the data can be loaded into GTPack by means of **GTPHMPBFields**.³⁾ *Mathematica*'s **Import** command is at the heart of this input routine. Examples of eigenmodes calculated by means of MPB can be found in Section 11.2.

In the two-dimensional case the two linear independent polarizations decouple, thus only one field component, i.e., a scalar field, has to be considered. A visualization in the three-dimensional case is more involved. The MPB documentation advises use of vis5d+ [228], a visualization program for scientific data. Other viewers like ParaView [229] can be used if the data is transformed into an appropriate format. In case of MPB output the use of h5tovtk⁴⁾ transforms the HDF5 datasets to a VTK format that can be plotted by ParaView. In the case of 3D data it is of course possible to load the data by means of **Import** into a *Mathematica* Notebook and use standard *Mathematica* commands for the visualization. This avoids the use of external viewers.⁵⁾

C.3

Comparison of Calculations with MPB and Mathematica

In Section 12.2, the photonic band structure for dielectric spheres in air arranged in a simple cubic lattice calculated by means of MPB and GTPack have been compared. In the GTPack calculation of the bands 1419 plane waves have been used. Thus, the calculation of band structures or densities of states for three-dimensional systems with *Mathematica* becomes time consuming.

Calculations can be performed more efficiently by submitting such long-lasting calculations into the background. The corresponding *Mathematica* commands have to be put in an input file. The corresponding calculation can be submitted as a background job with

```
math -noprompt -script input.m > output & (C.4)
```

3) See the documentation of **GTPHMPBFields** for details.

4) Part of the package h5utils.

5) See MPB_Import_3D.nb for example.

As an example, the input file for the calculation of the band structure for the example of dielectric spheres on a simple cubic lattice in air, as discussed in Section 12.2, is given here.

```
Needs["GroupTheory"]

(* cluster size for G-vectors, number of bands *)
cut=12;nbnd=20;

(* k-path in Brillouin zone *)
kp = {{0., 0., 0.}, {0., 0., .5}, {.5, .5, .5}, {0., .5, .5}, {0., 0., 0.}}, {"Gamma", "X",
"M", "R", "Gamma"}; kpts = GTBZLines[kp, {15, 15, 15, 15}];

(* reciprocal lattice vectors *)
basvec={{1.,0.,0.},{0.,1.,0.},{0.,0.,1.}};

(* permittivity – structural data *)
ra = 0.3; structure = {"Sphere", 13., {4 Pi/3 ra^3, ra, 0, 0, 0}, {0, 0, 0}}; eback = 1;

(* calculation of bands *)
bands=GTPbBandsObjects[structure,eback,basvec,cut,kpts,nbnd,
GODCMethod->"MatrixInverse"];

(* results to file *)
bands >> "bands.dat"
Exit
```

Appendix D

Technical Remarks on GTPack

D.1

Structure of GTPack

Related to the functionality of the modules, GTPack is divided into various subpackages as shown in Figure D.1. The subpackages can be assembled into three groups: “basic functionality,” “structure,” and “applications.” The subpackages belonging to the class of “basic functionality” are *Auxiliary.m*, *Basic.m*, *Install.m*, and *RepresentationTheory.m*. The package *Auxiliary.m* contains modules that are either needed by GTPack or extend the general *Mathematica* language. For example, tesseral harmonics (Appendix A.2) were added and also the Cartesian form of tesseral and spherical harmonics was implemented. Furthermore, the package contains modules for the handling of quaternions, the calculation of GAUNT coefficients, DIRAC matrices, or SU(2)-rotation matrices, to name but a few. The package *Basic.m* concentrates on general abstract group theory and, e.g., provides modules for the calculation of classes, multiplication tables, left and right cosets, and several logical commands to check for groups, Abelian groups, subgroups, or invariant subgroups. Modules needed for basic representation theory are contained in the package *RepresentationTheory.m*. This package comprises the calculation of character tables, handling of irreducible representations, the calculation of CLEBSCH–GORDAN coefficients, etc. Modules for the installation of point and space groups or symmetry elements can be found in *Install.m*. The content of these packages is mainly covered within Chapters 2–5.

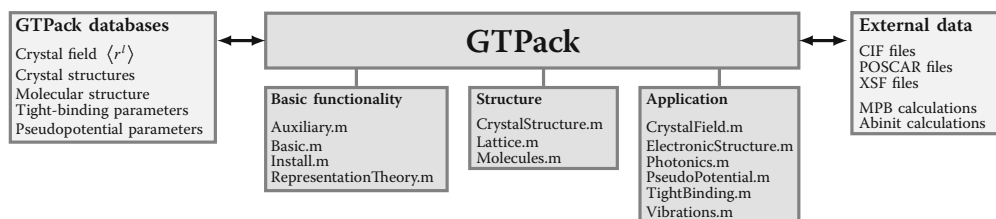


Figure D.1 Illustration of the subpackage structure of GTPack, its interaction with external databases, and interface to external ab initio software.

The second class “structure” consists of *CrystalStructure.m*, *Lattice.m*, and *Molecules.m*. Within *CrystalStructure.m*, modules for loading, saving, and handling of crystal structures can be found. Modules with similar functionality but specialized on molecules are contained within *Molecules.m*. The construction and manipulation of atomic clusters as well as several commands for dealing with the reciprocal space are summarized in the package *Lattice.m*.

As explained within Parts Two to Four, GTPack contains packages for particular applications in solid-state physics and photonics. The third class “applications” contains the subpackages *CrystalField.m*, *ElectronicStructure.m*, *Photonics.m*, *PseudoPotential.m*, *TightBinding.m*, and *Vibrations.m*. The crystal field package *CrystalField.m* is capable of automatically generating crystal field Hamiltonians (see Section 7.4). Furthermore, it contains the generation of standard operator equivalents like STEVENS [113] and BUCKMASTER–SMITH–THORNLEY [112] operators. GTPack also allows for electronic structure calculations for periodic systems, i.e., crystals, in the framework of the tight-binding and the pseudopotential approximation as discussed in Chapter 9. Modules to construct two- and three-center tight-binding Hamiltonians are summarized in *TightBinding.m*, whereas modules for the pseudopotential approximation are contained in *PseudoPotential.m*. The calculation of band structures, density of states, as well as the symmetry analysis of eigenstates is independent of the underlying model Hamiltonian. Therefore, such commands are contained within the general package *ElectronicStructure.m*. In the framework of plane waves it is also possible to calculate the band structure of photonic crystals as discussed in Part Three. The necessary modules for the construction of the master equation for various geometrical objects can be found in the package *Photonics.m*. Commands for the investigation of phonons or molecular vibrational modes are contained within *Vibrations.m* (Chapter 13).

As explained in Appendix B, GTPack is capable of incorporating data from databases, for example, for tight-binding parameters, crystal field parameters, and crystal structures. The interaction of such databases with GTPack is illustrated on the left-hand side of Figure D.1. For distinction, special file extensions were introduced, like **.parm* and **.struc*. These databases can be easily created, extended and modified by the user. Furthermore, GTPack includes commands for the interaction with external data formats and ab initio software. For example, this concerns the import and export of structural data files **.cif* [230], **.xsf* [149], and *POSCAR* [231] and the output of the programs MIT Photonic Bands – MPB [174, 175].

D.2

Installation of GTPack

The installation of the *Mathematica* group theory package GTPack follows the general line of installing packages within *Mathematica*. The package GTPack itself can be downloaded at <http://gtpack.org>. After decompressing the downloaded

file, the content of the package has to be copied to the application folder of *Mathematica* within the base directory. At this point the user has the choice of making the package available for all users of the computer or only for her- or himself, respectively.

1. If the package should be available for all users of the computer, open a *Mathematica* notebook and type **\$BaseDirectory**.
2. If the package should be available exclusively for the current user of the computer, open a *Mathematica* notebook and type **\$UserBaseDirectory**.

According to the path of the base or user base directory (called `$dir` in the following), the folder containing GTPack needs to be copied to the directory `$dir\Applications`. Afterwards, the package and the documentation are available. The package itself can be loaded within a *Mathematica* notebook by typing `Needs["GroupTheory"]`.

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Index

a

- approximation
 - adiabatic 310
 - BORN–OPPENHEIMER 310
- augmented matrix 25

b

- band gap
 - photonic 254
- band structure
 - Cu 199
- basis
 - function 107, 114
 - of group 36
 - rank of 36
 - reciprocal 135, 136
- binary rotation 15
- BLOCH
 - ansatz 135, 142
 - function 198, 201, 205, 206, 210, 217, 227, 231
 - theorem 135
 - wave 135
- block diagonal 88, 89
- BORN–OPPENHEIMER approximation 310
- boundary condition
 - BORN–VON KÁRMÁN 134
 - periodic 134
- BRAGG grating 253
- BRAVAIS lattice 311
- BRILLOUIN zone 138

c

- character 94
 - projection operator 107
 - system 94, 98, 115
 - table 98, 187
- chiral
 - angle 76
 - vector 76

- cif-files 64, 66
- class 40, 98
 - multiplication 41
- CLEBSCH–GORDAN
 - coefficients 89, 112, 115, 117, 119, 120, 123, 155, 160, 172, 173
 - sum 88–90, 92, 114, 117, 192
- compatibility relation 201
- conical transformation 19
- coset 43
 - representatives 43, 126
- crystal
 - photonic 253, 254
- crystal field 98, 156
 - expansion 160, 161
 - Hamiltonian 160
 - operators 164
 - operators (BUCKMASTER–SMITH–THORNLEY) 165
 - operators (STEVENS) 166
 - operators (WYBOURNE) 165
 - parameter 161

d

- degeneracy 156
- density functional theory 310
- dielectric atom 261
- direct product 48
- dynamical matrix 311
 - FOURIER transform 312
- dynamical symmetry 3

e

- element
 - conjugate 40
 - self-adjoint 41
- empty lattice test 270
- endomorphism 38
- equivalence relation 39
- Euclidian group 25

- EULER angles 16
- EULER–RODRIGUES parameter 20
- f*
- factor
 - group 46
- FERMAT's theorem 36
- FERMI
 - energy 231
 - surface 236
- filling factor 262
- FINDSYM 64
- force constant matrix 311
- form factor
 - pseudopotential 228
- g*
- generator 36
- GIBBS free energy 322
- graphene nanoribbon 238
- group 34
 - center of 41
 - composite 45
 - conjugate 66
 - continuous 34
 - covering 41
 - direct product 48
 - double 183, 186
 - finite 34
 - infinite 34
 - LIE 35
 - little 125, 142, 145
 - normalizer of 41
 - of $\mathbf{k}$ 138
 - of SCHRÖDINGER equation 154
 - order 35
 - semidirect product 49
 - semisimple 45
 - simple 45
 - space 62
 - super- 41
 - translation 59
- GTPack
 - GO XII
 - GODiagonal 115
 - GOHarmonics→“Real” 336
 - GOIrepNotation 101, 102, 157
 - GOPhotonic 312
 - GOProjection 204
 - GOREality 194, 195
 - GOREpresentation 183, 185
 - GOSpecMode 308
 - GOTable 62
 - GOTbLattice 215
 - GOVectorFields 291
 - GSMPBBands2D 341
 - GSMPBBands3D 341
 - GT XII
 - GTAbelianQ 34–36
 - GTAdjacencyMatrix 236, 242, 243
 - GTAllSymbols 52, 54
 - GTAngularMomentumChars 154, 156, 158, 334
 - GTAngularMomentumRep 84, 85, 334
 - GTBandsPlot 341
 - GTBandsPlotImprove 230, 234, 276, 292
 - GTBandStructure 210, 215, 216, 230, 312, 314, 315
 - GTBravaisLattice 137, 141, 146
 - GTBSTOperator 157, 166
 - GTBSTOperatorElement 157, 166
 - GTBuckyBall 75, 80
 - GTBZMPBPointMesh 342
 - GTBZPath 137, 141, 199, 215, 230
 - GTBZPointMesh 342
 - GTCartesianSphericalHarmonicY 333
 - GTCartesianTesseralHarmonicY 108, 296, 298, 336
 - GTCenter 39, 41, 42
 - GTCFDatabaseInfo 157, 167
 - GTCFDatabaseRetrieve 157, 167
 - GTCFDatabaseUpdate 157, 167
 - GTChangeRepresentation 183–186
 - GTCharacterTable 94, 98, 99, 101, 105, 115, 119, 157, 187, 188, 193–195, 200
 - GTCharacterTableOfK 143, 146, 147
 - GTCharProjectionOperator 105, 108, 109, 112, 283, 284, 288, 292
 - GTClasses 39–42, 104
 - GTClassMult 39
 - GTClassMultTable 39, 41, 42
 - GTClebschGordanCoefficients 112, 117–120, 173
 - GTClebschGordanSum 88, 90, 92
 - GTClebschGordanTable 112, 117, 119
 - GTCluster 210, 215, 219, 230, 248, 321
 - GTCompatibility 198, 202, 203, 279, 283, 284
 - GTConjugacyClass 39
 - GTConjugateElement 39, 40
 - GTCrystalField 162, 163
 - GTCrystalFieldExpansion 157
 - GTCrystalFieldParameter 157, 163
 - GTCrystalFieldSplitting 154, 157, 158
 - GTCrystalSystem 59
 - GTCyclicQ 36

- GTDensityOfStates 210, 314, 342
- GTDensityOfStatesPlot 342
- GTDensityOfStatesRS 236, 243
- GTDirectProductChars 112, 115, 117, 119, 190, 330
- GTDirectProductRep 112, 113, 115, 116, 120
- GTEulerAnglesQ 11, 16, 17
- GTFermiSurface 236
- GTFermiSurfaceCut 236, 237
- GTFermiSurfaceXSF 236, 237
- GTFindStateNumbers 236, 244
- GTGauntCoefficient 157, 163, 164
- GTGenerators 33, 36, 37, 58
- GTGetEulerAngles 11, 18
- GTGetIrep 88, 90, 91, 93, 108, 111, 115, 209
- GTGetIrepMatrix 221
- GTGetMatrix 13, 185, 186
- GTGetStructure 210, 228
- GTGetSU2Matrix 25, 30, 31
- GTGetSubGroups 34, 36, 42, 43
- GTGetSymbol 80
- GTGroupConnection 52, 59, 61
- GTGroupFromGenerators 33, 36, 37, 58, 78, 184, 186
- GTGroupGlp 210, 220
- GTGroupHierarchy 52, 59
- GTGroupNotation 52, 59
- GTGroupOfK 137–140
- GTGroupOrder 34, 35
- GTGroupQ XII, 34, 35
- GTHamiltonianList 210
- GTHamiltonianPlot 210, 215, 245, 248
- GTIcosahedronAxes 75, 80, 81
- GTImportCIF 67, 68, 339
- GTInstallAxis 52, 54, 55, 78
- GTInstallGroup 33–36, 56, 64, 65, 85, 87, 139, 146, 183, 185–188
- GTInstallStructure 339
- GTInvSubGroupQ 39, 45
- GTInvSubGroups 39, 45, 70
- GTIrep 94, 103, 104, 115, 119, 156, 158, 173, 190, 191, 203
- GTIrepDimension 88, 90, 91
- GTLatCluster 69, 288
- GTLatShells 69, 288
- GTLeftCosets 39, 44, 45
- GTLoadStructures 210, 228
- GTMagnetic 69, 70, 72
- GTMolChemicalData 301, 302, 339
- GTMolDatabaseInfo 301, 303
- GTMolDatabaseUpdate 301
- GTMolGetMolecule 203, 208, 301
- GTMolPermutationRep 203, 207, 208, 303
- GTMolToCluster 301, 339
- GTMPBBands 273
- GTMultTable 34–36
- GTNormalizer 39, 41, 43
- GTNumberOfIreps 88, 90, 91, 93
- GTOrderOfElement 34, 35
- GTPhBandsObjects 292
- GTPhCuboid 260
- GTPhDCObjects 260
- GTPhDCPixel 260
- GTPhEllipticRod 260
- GTPhFields 276
- GTPhMaster 270
- GTPhMasterObjects 270, 275
- GTPhMasterPixel 270, 275
- GTPhMPBBands 270, 341
- GTPhMPBFields 276, 277, 281, 282, 343
- GTPhPermittivityMatrix 260, 270
- GTPhPixelSmooth 260
- GTPhPixelStructure 260, 263, 264, 266
- GTPhPrismaticRod 260
- GTPhRodSmooth 260, 266
- GTPhShowStructure 260, 263, 264
- GTPhSlab 260
- GTPhSlabSmooth 260, 266
- GTPhSphere 260
- GTPhSymmetryAnalysis 292
- GTPhSymmetryBands 276–278
- GTPhSymmetryField 276, 277, 281, 282
- GTPhSymmetryPoint 276, 277
- GTPhUncoupledBands 283, 285
- GTPlotStateWeights 236, 244
- GTPlotStructure2D 210, 215
- GTPointGroups 52, 59, 61
- GTProductGroup 48, 49
- GTProductGroupQ 48, 49
- GTProjectionOperator 105, 108, 109, 209
- GTPwDatabaseInfo 227, 228
- GTPwDatabaseRetrieve 227, 228
- GTPwDatabaseUpdate 227, 228
- GTPwDatasetRetrieve 229
- GTPwEmptyLattice 291
- GTPwEmptyLatticeIrep 270–273, 288
- GTPwHamiltonian 227, 229, 230
- GTPwPrintParmSet 227, 229
- GTPwSymmetrizePW 203–205
- GTQAbs 11, 23
- GTQConjugate 11, 23
- GTQInverse 11, 22, 23
- GTQMultiplication 11, 21, 22
- GTQPolar 11, 23

- GTQuaternionQ 11, 21, 22
 - GTQuotientGroup 46, 47
 - GTQuotientGroupQ 46, 47
 - GTReadFromFile 210
 - GTReality 193, 194
 - GTReciprocalBasis 136, 137, 139, 146
 - GTRegularRepresentation 84–87, 96
 - GTReinstallAxes 13, 14
 - GTReinstallAxes 11
 - GTReorderMatrix 245
 - GTRightCosets 39, 44, 45
 - GTShells 210, 215, 219, 230, 240, 248
 - GTShellVectorsQlp 210, 220
 - GTShowSymmetryElements 52, 58, 320
 - GTSOCSplitting 189, 191, 192, 246
 - GTSpaceGroups 62, 64, 65
 - GTSpinCharacters 189–191
 - GTStarOfK 137–140
 - GTStevensOperator 157, 166, 169
 - GTStevensOperatorElement 157, 166, 169
 - GTStevensTheta 157, 166
 - GTSU2Matrix 25, 29, 30
 - GTSubGroupQ 34, 36
 - GTSymmetrizedProductChars 327, 328, 330
 - GTSymmetryBasisFunctions 210, 218, 296–298, 326
 - GTSymmetryElementQ 75, 77, 80, 320, 321
 - GTSymmetrySingleBand 230
 - GTTableToGroup 33, 36–38, 85
 - GTTbDatabaseInfo 210, 337
 - GTTbDatabaseRetrieve 210
 - GTTbHamiltonian 210, 215
 - GTTbHamiltonian3C 224
 - GTTbHamiltonianOnsite 230
 - GTTbHamiltonianRS 236, 243
 - GTTbIntegralRules 210, 221–223
 - GTTbMatrixElement 210, 212, 213, 338
 - GTTbMatrixElement3C 210, 221–223
 - GTTbNumberOfIntegrals 210, 220
 - GTTbParmToRule 210, 230, 231, 241
 - GTTbReadWannier90 210, 226
 - GTTbRealSpaceMatrix 236, 242
 - GTTbSpinMatrix 225
 - GTTbSpinOrbit 210, 225
 - GTTbSymbol3C 222, 223
 - GTTbSymmetryBands 230, 232, 235
 - GTTbSymmetryPoint 230, 232
 - GTTbSymmetrySingleBand 232
 - GTTbTubeBands 236
 - GTTbWannier90Hamiltonian 210, 226
 - GTTesseralHarmonicY 335
 - GTTPhMasterObjects 270
 - GTTransformationOperator 111
 - GTTransformQlp 210
 - GTTransformToQlp 221
 - GTTubeBands 239
 - GTTubeParameters 75, 76, 239
 - GTTubeStructure 75, 77, 78, 238
 - GTVarList 221
 - GTVectorRep 302
 - GTVibDisplacementRep 302, 303
 - GTVibDynamicalMatrix 310, 312–314
 - GTVibLatticeModes 310, 316, 317
 - GTVibModeSymmetry 302, 305, 306, 309, 316
 - GTVibSetParameters 310, 312, 313, 315, 316
 - GTVibSpectroscopy 302, 308, 309
 - GTVibTbToPhonon 310, 315, 316
 - GTVibTbToPhononRule 310, 315, 316
 - GTVoronoiCell 68, 69, 137, 139, 141, 236
 - GTWavefunctionPlot 210
 - GTWhichAxes 11, 13
 - GTWhichRepresentation 183
 - GTWignerCharProjectionOperator 334
 - GTWignerProjectionOperator 105, 206, 334, 336
 - GTWriteToFile 210
- h*
- H₂O 308
 - HAMILTON operator 152–154, 156, 159, 161, 196
 - Hamiltonian 152, 153
 - high symmetry
 - lines 139
 - points 139
 - holohedry 59
 - homomorphism 38, 178
- i*
- improper rotation 13
 - index 43
 - induced dipole moment 307
 - infrared activity 307
 - integral
 - on-site 212
 - three-center 212
 - two-center 212
 - invariant polynomial 326
 - inversion 6
 - irreducible tensor operator 121
 - isomorphism 38

k

- kinetic energy 152
- KORRINGA–KOHN–ROSTOKER method 294
- k-space 133

l

- LAGRANGE's theorem 36
- lattice 59
 - real-space 136
 - reciprocal 136
- LEGENDRE polynomial 160
- lemmas of SCHUR 91
- LIE group 35
- LÖWDIN transformation 211

m

- master equation 254, 256, 270, 293
- materials equations 255
- Mathematica
 - \$BaseDirectory 347
 - Import 343
 - MatrixPower 32
 - Method 111
 - MonomialList 326
 - PauliMatrix 32
 - Q XII
 - RotationMatrix 30, 87
 - SphericalHarmonicY 332
 - SphericalPlot3D 335
 - ThreeJSymbol 166
 - \$UserBaseDirectory 347
 - WignerD 333
- matrix
 - representation 88, 89
- matrix element
 - reduced 122
 - theorem 156
- MAXWELL's equations 254, 256, 257
- method
 - of induction 123
 - pseudopotential 227
- MIE scattering problem 294
- multiplication table 35

n

- nanotube
 - armchair 77, 238
 - chiral 240
 - chiral angle 76
 - chiral vector 76
 - single-walled 75
 - translational vector 76
- zigzag 238

notation

- BETHE 99
- BOUCKAERT 99
- international 64
- MULLIKEN 99, 100
- SCHÖNFLIES 52, 64

o

- OPECHOWSKI theorem 186
- orbit 144
- order
 - of group 35
 - of group element 35
- order parameter 323
- orthogonality theorem 92, 107
 - characters 97

p

- PAULI
 - equation 28, 178, 183, 196, 253, 257
 - matrices 28, 178
 - vector of matrices 28
- PBS 270
- perturbation theory
 - time dependent 169
 - time independent 157
- photonic band gap 274
- photonic crystal 253
- point
 - charge model 161
 - defect 279
- potential
 - external 152
- product
 - direct 48, 113
 - KRONECKER 113
 - semidirect 49, 142
- projection operator 107, 108
- proper rotation 13
- pseudopotential 227
 - empty core 228
 - form factor 228
- HEINE–ABARENKOV 228
- pseudo-wave function 227

q

- quaternion 20
 - pure 20
 - real 20
 - unit 21
- quotient
 - group 46
 - set 46

r

RAMAN

- activity 307
- polarisability tensor 307

reflection 15

- lines 6

representation 84

- allowed 146
- direct product 113, 114, 116–118
- displacement 304
- equivalent 89
- extra- 187
- faithful 85
- induced 123
- irreducible 89, 98, 103, 107, 108, 115, 121–123, 127, 142, 143, 154, 156, 159, 186
- matrix 84
- permutation 302
- reducible 89
- regular 103
- similar 89
- theory 84
- unitary 84
- vector 304

rotation 6

- binary 15
- improper 13
- pole 18
- proper 13

rotoreflection 15

s

SALC 206

SCHÖNFLIES, A.M. 52

SCHRÖDINGER

- equation 133, 134, 136, 151, 152, 154–156, 159, 161, 170, 177, 178, 183, 189, 195–198, 203, 210, 211, 219, 254, 257

- equation, group of 154

SCHRÖDINGER equation

- stationary 152

selection rules 169

semidirect product 49, 124

single-walled carbon nanotubes 238

site symmetry 66

SO(3) 178

space group 62

- irreducible representations 230
- nonsymmorphic 62, 77, 143
- symmorphic 62, 77, 142

spherical harmonics 294

spin space 178

spin–orbit coupling 178, 180, 182, 189

star of **k** 138

structure

- perovskite 248
- zinc blende 240

SU(2) 178

subgroup 6, 36

- conjugate 41, 66
- diagonal 113
- invariant 44, 63

subspace 114

supergroup 41

symmetry

- adapted linear combination 206
- group 6
- time-reversal 196

t

tight-binding

- real-space approximation 240
- two-center approximation 212

transformation matrix 89

u

uncoupled bands 283

unit cell 61

- nonprimitive 61
- primitive 61

v

VAN HOVE singularity 285

vector

- field 254
- spherical harmonics 294

VORONOI cell 68

w

WANNIER

- function 226
- transformation 226

wannier90 226

water 308

WIGNER 3/-symbol 166

WIGNER–ECKART theorem 120–123, 155, 160, 172, 203, 307, 308

WIGNER–SEITZ cell 65

x

XCrysDen 237

XeF₄ 308

xenontetrafluoride 308